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# COMPTES RENDUS

## (DOKLADY)

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*MATHÉMATIQUES*

# SUR LES CONDITIONS POUR QU'UN SYSTÈME DE POLYNÔMES ORTHOGONAUX AVEC UN POIDS SOIT FERMÉ

Par M. KELDYCH

*(Présenté par S. L. Soboleff, de l'Académie, le 20. XII. 1940)*

1. Soit $D$ un domaine univalent et simplement connexe dans le domaine de la variable complexe $z$ et $h(z)$ une fonction positive telle que l'intégrale

$$\iint_D h(z)\,d\sigma < +\infty \tag{1}$$

est finie et d'ailleurs $h(z)$ est bornée inférieurement sur chaque ensemble fermé contenu dans le domaine $D$. Par définition, une fonction $f(z)$ holomorphe à l'intérieur de $D$ appartient à la classe $H_D$, si l'intégrale

$$\iint_D h(z)\,|f(z)|^2\,d\sigma \tag{2}$$

est finie.

Le système de tous les polynômes de la variable complexe $z$ est dit fermé dans le domaine $D$ par rapport au poids $h(z)$, si pour chaque fonction appartenant à la classe $H_D$ la borne inférieure de l'intégrale

$$\iint_D h(z)\,|f(z)-P(z)|^2\,d\sigma \tag{3}$$

s'annulle sur la famille de tous les polynômes $P(z)$.

Si le système de tous les polynômes est fermé par rapport au poids $h(z)$, les polynômes orthogonaux avec le poids $h(z)$ dans le domaine (obtenus par l'orthogonalisation des puissances de $z$) possèdent la plupart des propriétés élémentaires des séries orthogonales avec le poids $h(z)=1$, et, en particulier, chaque fonction de classe $H_D$ peut être développée en une série de polynômes orthogonaux qui converge uniformément à l'intérieur du domaine.

2. Dans le cas où le domaine $D$ est un cercle et le poids $h(z)$ est égal au carré du module d'une fonction $\varphi(z)$, analytique à l'intérieur d'un cercle, Schaguinjan a étudié le problème, à savoir si le système des polynômes est fermé. Il a obtenu une série de critères suffisants, exprimés comme propriétés de la fonction $\varphi(z)$ pour que le système soit fermé.

On peut montrer que *dans le cercle* $|z|<1$ *il existe des poids égaux aux modules de fonctions analytiques et pour lesquels le système des polynômes n'est pas complet.*

En qualité d'un tel poids on peut choisir la fonction

$$h(z)=|e^{\frac{z+1}{z-1}}|.$$

Signalons encore ici la condition suivante qui est suffisante pour que le système des polynômes soit complet dans le cercle.

*Si le poids $h(z)$ conserve une valeur constante sur chaque circonférence concentrique $h(z)=\chi(|z|)$, alors le système des polynômes est complet dans le cercle.*

Soit $h(z)$ un poids défini dans le domaine $D$, $z=\varphi(\zeta)$ — la fonction qui réalise la représentation conforme du cercle sur le domaine $D$. Nous dirons que le poids $h(z)$ vérifie la condition $A$, si dans le cercle $|\zeta|<1$ le système des polynômes est fermé avec le poids $h[\varphi(\zeta)]$. En particulier, si $h(z)$ conserve des valeurs constantes sur les lignes de niveau, $h(z)$ vérifie la condition $A$.

3. Il est connu que pour $h(z)=1$ le système des polynômes ne sera pas complet dans chaque domaine connexe. Par exemple, dans le domaine $K_0$ que l'on obtient en enlevant du cercle $|z|<1$ le rayon $\arg z=0$, le système des polynômes n'est pas fermé.

On a la proposition suivante.

Théorème. *Dans chaque domaine simplement connexe on peut construire un poids vérifiant les conditions du § 1 et pour lequel le système des polynômes est fermé.*

Nous n'allons qu'indiquer la démonstration. Soit $\zeta=\omega(z)$ la fonction réalisant la représentation conforme de $D$ sur le cercle $|\zeta|<1$; $C_\rho$ — les lignes de niveau $|\omega(z)|=\rho$; $D_\rho$ — le domaine borné par la ligne $C_\rho$; $\rho_0, \rho_1, \ldots, \rho_n, \ldots$ une suite de nombres tendant vers l'unité. Nous poserons $h(z)=\alpha_n$ dans le domaine $D_{\rho_n}-D_{\rho_{n-1}}$, et d'ailleurs la suite décroissante des nombres $\alpha_0, \alpha_1, \ldots, \alpha_n, \ldots$ se construit de la manière suivante. On pose $\alpha_0=1$. Supposons que $\alpha_0, \alpha_1, \ldots, \alpha_{n-1} \ldots$ sont déjà définis, et définissons $\alpha_n$. A cet effet construisons le système des polynômes

$$P_{n,0}(z),\ P_{n,1}(z),\ \ldots,\ P_{n,n}(z)$$

vérifiant l'inégalité

$$\iint\limits_{D_{n-1}} |[\omega(z)]^k \omega'(z) - P_{n,k}(z)|^2\, d\sigma < \frac{1}{2^n} \quad (k=0, 1, 2, \ldots, n);$$

en qualité de $\alpha_n$ prenons le plus grand nombre vérifiant les inégalités

$$\alpha_n \leqslant \alpha_{n-1},\ \alpha_n \iint\limits_{(D-D_{n-1})} |P_{n,k}(z)|^2\, d\sigma \leqslant \frac{1}{2^n} \quad (k=0, 1, \ldots, n).$$

Il est facile de voir que pour le poids ainsi construit et pour toutes les fonctions de la forme $[\omega(z)]^k \omega'(z)$ la condition

$$\inf \iint\limits_D |[\omega(z)]^k \omega'(z) - P(z)|^2 h(z)\, d\sigma = 0 \qquad (4)$$

pour que le système soit fermé, est vérifiée.

Le poids ainsi construit vérifie la condition $A$; c'est pourquoi il est facile de déduire de (4) que le système est fermé par rapport à une fonction quelconque de classe $H_D$.

4. Dans un domaine simplement connexe arbitraire on ne peut pas construire un poids borné inférieurement dans tous le domaine, tel que le système des polynômes soit fermé par rapport à ce poids. Le théorème suivant permet d'évaluer l'ordre de décroissement du poids quand on s'ap-

proche de la frontière, ordre qui est en général nécessaire pour que le système soit complet.

Théorème. *Soit $D$ un domaine simplement connexe. Si le poids $h(z)$ vérifie la condition* A *et*

$$\liminf_{d\to 0} \frac{\ln\ln\ln \frac{1}{h(z)}}{\ln \frac{1}{d}} > 2$$

*où $d$ est la distance du point $z$ à la frontière du domaine $D$, alors le système des polynômes est fermé dans $D$ par rapport au poids $h(z)$.*

En particulier, il suit de cette proposition que pour le poids

$$h(z) = e^{-e^{\frac{1}{(1-|\omega(z)|)^{\alpha}}}}, \quad \alpha > 4$$

où $\omega(z)$ est la fonction réalisant la représentation de $D$ sur le cercle $|\zeta| < 1$, le système des polynômes sera complet.

La proposition suivante montre que l'évaluation donnée dans le théorème précédent ne peut pas être essentiellement améliorée.

Théorème. *Il existe un domaine simplement connexe tel que pour chaque poids vérifiant la condition*

$$\limsup_{d\to 0} \frac{\ln\ln\ln \frac{1}{h(z)}}{\ln \frac{1}{d}} < 2$$

*le système des polynômes n'est pas fermé.*

On peut obtenir un exemple d'un domaine pareil en enlevant du cercle unitaire la spirale

$$\rho = 1 - \frac{1}{\ln \varphi} \quad (\pi \leqslant \varphi < +\infty).$$

Remarquons encore que dans le cas du domaine $K_0$ (voir le § 3) pour que le système soit fermé il suffit que le poids vérifie la condition A, et que sur le rayon $\arg z = 0$ on ait

$$\liminf_{d\to 0} \frac{\ln\ln\ln \frac{1}{h(z)}}{\ln \frac{1}{d}} > 1;$$

et dans le cas de l'inégalité

$$\limsup_{d\to 0} \frac{\ln\ln\ln \frac{1}{h(z)}}{\ln \frac{1}{d}} < 1$$

le système n'est pas fermé.

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*MATHEMATICS*

# AN EXTENSION OF LAGUERRE'S THEOREM ON THE ROOTS OF A TRANSCENDENT FUNCTION

By M. VERJBINSKY

*(Communicated by S. N. Bernstein, Member of the Academy, 24. XII. 1940)*

1. Laguerre (1), Polya (2) and Schur (3) have studied the question on the nature of the zeroes of the function $\Phi(x)=\sum_{\nu=0}^{\infty} a_\nu P(\nu) x^\nu$, the nature of the zeroes of the functions $P(\nu)$ and $f(x)=\sum_{\nu=0}^{\infty} a_\nu x^\nu$ being known.

The final result of the previous investigations was the theorem: If the functions $f(x)$ and $P(\nu)$ are integral transcendent functions of the genus not exceeding 1, the zeroes of $f(x)$ being real and of $P(\nu)$ real and negative, then the function $\Phi(x)$ has also only real zeroes.

The following two ways of generalization of this theorem are interesting. The function $f(x)$ is an integral transcendent function, the zeroes of which are not necessarily real, but lie in some definite region of the plane of the complex variable. The function $P(\nu)$ is an integral transcendent function, the complex zeroes of which have real negative parts. In both cases we are faced with the problem to find the region containing the zeroes of the function $\Phi(x)$. In this paper I shall restrict myself to the generalization of Laguerre's theorem only in one direction.

2. Let $f(x)=\sum_{\nu=0}^{\infty} a_\nu x^\nu = e^{c_0+c_1+x+\ldots+c_m x^m}\cdot\prod_{\mu}\left(1-\frac{x}{x_\mu}\right)e^{\frac{x}{x_\mu}+\ldots+\frac{x^m}{m x_\mu^m}}$ be an integral transcendent function of the complex argument $x=\sigma+it$ of the genus $m$. Let us introduce the function

$$f_N(x)=e^{c_0+c_1 x+\ldots+c_m x^m}\cdot\prod_{\mu=1}^{N}\left(1-\frac{x}{x_\mu}\right)e^{\frac{x}{x_\mu}+\ldots+\frac{x^m}{m x_\mu^m}}=\sum_{\nu=0}^{\infty} a'_\nu x^\nu.$$

Thus, we have $f(x)=\lim_{N\to\infty} f_N(x)$ and $a'_\nu \underset{N\to\infty}{\longrightarrow} a_\nu$.

Let us form a new function ($\gamma$ — constant): $f^*_N(x)=\sum_{\nu=0}^{\infty} a'_\nu(\nu+\gamma)x^\nu$;

it is evident that: $f_N(x)=x f_N(x)F_1(x)$, where $F_1(x)=\frac{\gamma}{x}+\frac{f'_N(x)}{f_N(x)}$.

The zeroes of $f^*_N(x)$ coincide with the zeroes of $F_1(x)$ and with the multiple zeroes of $f_N(x)$. The limit of the sequence of the functions $f^*_N(x)$ is the function $f^*(x)=\sum_{\nu=0}^{\infty} a_\nu(\nu+\gamma)x^\nu$.

Lemma 1. *The genus of the function $f^*(x)$ does not exceed that of the function $f(x)$.*

Proof. a) Using Cauchy's integral, the contour of integration being circle with the centre at the origin and the radius $r+1$, and making use of the principle of the maximum modulus, we obtain:

$$\max_{|x|\leqslant r} |f^{(k)}(x)| \leqslant (r+1) \max_{|x|=r+1} |f(x)|.$$

b) Since $f(x)$ is a function of the genus $m$, we have by Hadamard's theorem: $\max_{|x|\leqslant r} |f(x)| < e^{\beta+\varepsilon}$, where $m \leqslant \beta < m+1$ and $\varepsilon$ is arbitrarily small. Further: $\max |f^*(x)| \leqslant r \max |f'(x)| + |\gamma| \max |f(x)| < e^{r^{\beta+\varepsilon}}$ where $\varepsilon_1 = \varepsilon + \dfrac{\ln\left[\left(1+\frac{1}{r}\right)^{\beta+\varepsilon} + \frac{\ln 2r(r+1)}{r^{\alpha+\varepsilon}}\right]}{\ln r}$ is asymptotically arbitrarily small. By Hadamard's theorem, $f^*(x)$ is of the genus not exceeding $m$.

Lemma 2. *If the zeroes of the function $Q(x) = \sum_{s=0}^{\infty} c_s x^s$ lie inside some contour $\Gamma$ and $p$ is real, then the zeroes of the function $Q_1(x) = \sum_{s=0}^{\infty} c_s e^{ps} x^s$ lie inside the contour $\Gamma_1$ similar to $\Gamma$.*

3. Let us proceed to the discussion of the results obtained.

Theorem 1. *Let $f(x)$ be an integral transcendent function of the genus $0, \gamma > 0$. If the zeroes of $f(x)$ are situated inside a convex contour $C$ including the origin, the zeroes of $f^*(x)$ do not lie outside this contour either.*

Proof. Let us denote: $x = re^{i\theta} = re^{i(g-\alpha)}$; $x_\mu = r_\mu e^{i\theta_\mu} = r_\mu e^{i(g-\alpha_\mu)}$; $\gamma = \rho e^{i\lambda}$; $b_\mu$ is the distance between $x$ and $x_\mu$; $\sigma \cos g + t \sin g = h$ is the equation of the tangent to the contour $C$ ($h$ is the distance from the origin, $g$ is the angle of the normal with the axis $\sigma$). If $x$ and the contour $C$ lie on opposite sides of the tangent, then $|\alpha| \leqslant \frac{\pi}{2}$, $|\alpha_\mu| \leqslant \pi$ and $r \cos \alpha = h + \varepsilon$, $r_\mu \cos \alpha_\mu = h - \omega_\mu$, where $\varepsilon$ and $\omega_\mu$ are not negative. We have:

$$Re\, e^{ig} F_1(x) = \frac{\rho}{r} \cos(\lambda+\alpha) + \sum_{\mu=1}^{N} \frac{\varepsilon+\omega_\mu}{b_\mu^2} + \left(c_1 \cos g + \sum_{\mu=1}^{N} \frac{\cos \alpha_\mu}{r_\mu}\right) +$$

$$+ r\left(2c_2 \cos(2g-\alpha) + \sum_{\mu=1}^{N} \frac{\cos(2\alpha_\mu - \alpha)}{r_\mu^2}\right) + \ldots$$

$$\ldots + r^{m-1}\left(mc_m \cos(mg - \overline{m-1}\alpha) + \sum_{\mu=1}^{N} \frac{\cos(m\alpha - \overline{m-1}\alpha)}{r_\mu^2}\right).$$

The last expression shows, that if $f_N(x)$ is of the genus 0 and $\lambda = 0$, then for any $g$ $Re e^{ig} F_1(x) > 0$, since $x$ is separated from the origin by the tangent. Accordingly, the zeroes of $F_1(x)$ and hence of $f_N^*(x)$ are inside $C$. In virtue of the uniform convergence of the infinite product we conclude that the zeroes of $f^*(x)$ also lie inside the region $C$.

Theorem 2. *Let $f(x)$ be a function of the genus 0 and $P(\nu) = e^{k_0 + k_1 \nu} \cdot \prod_{\eta} \left(1 - \frac{\nu}{\nu_\eta}\right) e^{\frac{\nu}{\nu_\eta}}$ a function of the genus not exceeding one. Let the zeroes of $P(\nu)$ be real negative and satisfy the relation:*

$$k_1 = \sum \frac{1}{\nu_\eta} \geqslant 0. \qquad (1)$$

*If the zeroes of* $f(x)$ *are situated inside a convex contour* $C$ *including the origin, then the zeroes of the function* $\Phi(x) = \sum_{\nu=0}^{\infty} a_\nu P(\nu) x^\nu$ *are enclosed inside the same contour.*

Proof. Let us form functions of the form:

$$f^{n*}(x) = \sum_{\nu=0}^{\infty} a_\nu (\nu+\gamma_1)(\nu+\gamma_2) \dots (\nu+\gamma_n) x^\nu \quad (n = 1, 2, 3, \dots)$$

recurrently connected with each other by the relation:

$$f^{n*}(x) = x f^{1(n+1)*}(x) + \gamma_n f^{(n-1)*}(x).$$

According to lemma 1, the genus of all these functions does not exceed that of the function $f(x)$. Consequently, by induction follows from theorem 1 ($\gamma_1, \gamma_2, \dots, \gamma_n > 0$) that the zeroes of $f^{n*}(x)$ lie inside the contour including the zeroes of $f(x)$. The insertion of the exponential factor does not by lemma 2 and inequality (1) change the contour. The theorem is proved by passing to the limit $n \to \infty$.

Theorem 3. *Let* $f(x) = \sum_{\nu=0}^{\infty} a_\nu x^\nu$ *be a function of the genus not exceeding 1.* $a_\nu$ *real,* $\gamma > 0$. *Then the unreal zeroes of* $f^*(x)$ *are situated inside the circles, the ends of the diameters of which coincide with the complex conjugated zeroes of* $f(x)$.

Proof. Let $x = re^{i\theta}$. Since $a_\nu$ are real, the zeroes of $f(x)$ are pairwise conjugated: $x_\mu = r_\mu e^{i\theta_\mu}$, $\bar{x}_\mu = r_\mu e^{-i\theta_\mu}$; $b_\mu$ is the distance between $x$ and $x_\mu$; $b'_\mu$ is the distance between $x$ and $x_\mu$; $\Psi$ is the angle between the straight lines, connecting $x$ with $x_\mu$ and $x$ with $\bar{x}_\mu$; $\gamma = \rho e^{i\lambda}$. We have:

$$Im \sum_{\mu=1}^{N} \frac{re^{-i\theta} - r_\mu e^{-i\theta_\mu}}{b_\mu^2} = -t \sum_{\mu=1}^{N} \frac{\cos\psi}{b_\mu b'_\mu};$$

and so

$$Im F_1(x) = \frac{\rho}{r} \sin(\lambda - \theta) - t \sum_{\mu=1}^{N} \frac{\cos\psi}{b_\mu b'_\mu} +$$

$$+ r \sin\theta \left(2c_2 + \sum_{\mu=1}^{N} \frac{\cos 2\theta_\mu}{r_\mu^2}\right) + \dots + r^{m-1} \sin(m-1)\theta \left(m c_m + \sum_{\mu=1}^{N} \frac{\cos m\theta_\mu}{r_\mu^m}\right). \qquad (2)$$

As sign $t = \operatorname{sign} \sin\theta$, when $\lambda = 0$, it follows from (2) that since $f_N(x)$ is of the genus not exceeding 1, the unreal zeroes of $f_N^*(x)$ cannot lie outside the circles, the diameter ends of which coincide with the pairs of complex conjugated zeroes of $f_N(x)$. Passing to the limit $N \to \infty$, we obtain the theorem. Its validity is secured by the uniform convergence of the infinite product.

Theorem 4. *If* $2c_r + \sum_{\mu=1}^{N} \frac{\cos 2\theta_\mu}{r_\mu^2} \leqslant 0$, *then theorem* 3 *extends to the functions* $f(x)$ *of the genus not exceeding two.*

The proof follows from (2).

Theorem 5. *Let* $f(x)=\sum_{\nu=0}^{\infty} a_\nu x^\nu$ *be a function of genus not exceeding* 1. *where* $a_\nu$ *are real. Let* $P(\nu)$ *be a polynomial of degree* $n$ *with real coefficients and negative zeroes. Then the unreal zeroes of the function* $\Phi(x)=\sum_{\nu=0}^{\infty} a_\nu P(\nu)\, x^\nu$ *are situated inside the ellipses, the small axes of which abut on pairs of conjugated zeroes of* $f(x)$ *and the relation of the axes is equal to* $\sqrt{n}$.

Proof. We have: $P(\nu)=A\prod_{i=1}^{n}(\nu+\gamma_i)$, where $\gamma_i<0$. Let us form a sequence of functions $f^*(x), f^{2*}(x)\ldots, f^{n*}(x)$, connected by the recurrence relation: $f^{k*}(x)=xf'^{(k-1)*}(x)+\gamma_k f^{(k-1)*}(x)$.

By lemma 1 the genus of all these functions does not exceed that of $f(x)$. Any point of each of the circles introduced into theorem 3 may prove to be a zero of $f^*(x)$. Then the unreal zeroes of $f^{2*}(x)$ lie inside the envelopes of families of circles, constructed on chords of the circles enclosing the zeroes of $f^*(x)$ parallel to the axis $t$ as on diameters. These envelopes are ellipses, the small axes of which connect pairs of corresponding conjugated zeroes, and the ratio of whose axes is $1:\sqrt{2}$. The proof is completed by induction.

Corollary. If $f(x)=\sum_{\nu=0}^{\infty} a_\nu x^\nu$ is a function of the genus not exceeding 1, and $a_\nu$ are real, then the unreal zeroes of $f^{(n)}(x)$ are situated inside the ellipses defined in theorem 5. This follows from theorem 5, when $\gamma_1=\gamma_2=\ldots=\gamma_n=0$.

Theorem 6. *Let* $f(x)=\sum_{\nu=0}^{\infty} a_\nu x^\nu$ *be a function of the genus not exceeding* 1 *with* $a_\nu$ *real. Let* $P(\nu)=e^{k_0+k_1\nu}\cdot\prod_\eta\left(1-\frac{\nu}{\nu_\eta}\right)e^{\frac{\nu}{\nu_\eta}}$ *be a function of the genus also not exceeding* 1, *having only negative zeroes, satisfying the condition*

$$k_1+\sum_\eta \frac{1}{\nu_\eta}\geqslant 0. \qquad (3)$$

*Then the zeroes of the function* $\Phi(x)=\sum_{\nu=0}^{\infty} a_\nu P(\nu)\, x^\nu$ *lie within the strip, symmetrical with respect to the axis* $\sigma$ *and including the zeroes of* $f(x)$.

Proof. Taking the result of theorem 5, we pass to the limit $n\to\infty$. Further we insert an exponential factor, which is possible on account of lemma 2 and inequality (3).

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*MATHÉMATIQUES*

# SUR LES ANNEAUX SEMI-ORDONNÉS

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*(Présenté par A. N. Kolmogoroff, de l'Académie, le 7. I. 1941)*

Dans le présent article nous considérons les conditions pour qu'un anneau semi-ordonné soit en similitude isomorphe avec l'anneau de toutes les fonctions réelles continues sur un certain bicompact. Une correspondance est nommée similitude isomorphe, si elle est biunivoque et conserve les opérations d'addition et de multiplication ainsi que les relations d'ordre. Le théorème III a été démontré précédemment par Stone (1) dans la condition supplémentaire $x^2 > \theta$ quel que soit $x \in R$.

D'ailleurs, Stone a supposé a priori que l'anneau $R$ est commutatif. Ainsi qu'il résulte de notre article, cette condition est une conséquence des précédentes. Stone utilise dans sa démonstration la méthode des fractions continues. Notre méthode est proche à celle de Gelfand (2) qu'il a utilisé pour démontrer les théorèmes sur les anneaux normés, et elle diffère en ce que nous ne nous appuyons pas sur les théorèmes de la théorie des fonctions d'une variable complexe.

1. Soit $R$ un anneau avec une unité où l'on a introduit la multiplication par les nombres réels. Nous dirons qu'un anneau est *semi-ordonné*, si pour certains de ses éléments on a établi la relation $x > \theta$ ($\theta$ est le zéro de l'anneau) vérifiant les axiomes:

Axiome I. *Si* $x > \theta$, *on a* $x \neq \theta$.

Axiome II. *Si* $x > \theta$ *et* $y > \theta$, *on a* $x + y > \theta$.

Axiome III. *Si* $x > \theta$ *et* $\lambda > 0$ ($\lambda$ — *un nombre réel*), *on a* $\lambda x > \theta$.

Axiome IV. *Si* $x > \theta$ *et* $y > \theta$, *on a* $xy \geqslant \theta$.

Les éléments $x > \theta$ ($x \in R$) seront nommés *positifs*. Convenons d'écrire $x > y$, si $x - y > \theta$. Remarquons que si $x > y$ et $z > \theta$, on a $xz \geqslant yz$. Dans la suite nous allons imposer à l'anneau $R$ des restrictions supplémentaires.

Condition A. Pour chaque élément $x \in R$ il existe un nombre $t > 0$ tel que $-te < x < te$, où $e$ est l'unité de l'anneau.

Corollaire. Dans la condition A chaque élément $x \in R$ peut être présenté comme la différence de deux éléments positifs. Par exemple, $x = te - (te - x)$.

Condition B. Dans $R$ la condition A est remplie et d'ailleurs $\inf t \neq 0$ ($-te < x < te$). Désignons par $\rho_x$ la borne inférieure des nombres $te$, pour lesquels $x < te$.

Enfin formulons encore la condition C.

Condition C. Dans $R$ est remplie la condition $x \leqslant \rho_x e$.

Corollaire. Si $\rho_x = 0$ (respectivement $\rho_{-x} = 0$), alors il suit de la condition C que $x < \theta$ (respectivement $x > \theta$). Ainsi pour chaque $x$ l'un des nombres $\rho_x$ et $\rho_{-x}$ est non nul.

Pour abréger l'exposition, introduisons les définitions suivantes.

Définition I. Un élément $x > 0 (x \in R)$ sera nommé *intérieur*, s'il existe un nombre $t > 0$ tel que $tx > e$. Dans le cas contraire l'élément sera nommé *frontière*.

Remarque I. Si dans $R$ la condition C est remplie et s'il existe un élément $x \neq \lambda e$ ($\lambda$ est un nombre réel), alors $R$ contient un élément frontière. En effet, $\rho_x e - x = x_0$ sera un tel élément (si $\rho_x \neq 0$), et $x_0' = \rho_{-x} + x$ (si $\rho_{-x} \neq 0$).

Définition II. Un idéal $I$ de l'anneau $R$ qui est bilateral et non trivial (c'est-à-dire différent de $R$ et de 0) sera nommé *fondamental*, si de ce que $x$ est un élément de $I$ il suit nécessairement que chaque élément $y$, vérifiant la condition $0 < y < x$, appartient à $I$.

Remarque II. Soit $x_0$ un élément frontière et supposons que la condition A est remplie dans $R$. Alors l'ensemble $I_{x_0}$ des éléments $y$, vérifiant l'inégalité $-tx_0 < y < tx_0$ pour un certain $t$, forme un idéal fondamental. En effet, il est facile à voir que la somme et la différence de deux éléments de $I_{x_0}$ appartiennent à $I_{x_0}$. Ensuite, si $y \in I_{x_0}$ et $z > 0$, $z \in R$, alors $-tx_0 < y < tx_0$; donc

$$-\rho_z t x_0 \leqslant -tzx_0 \leqslant zy \leqslant tzx_0 \leqslant \rho_z t x_0, \quad \text{c'est-à-dire } zy \in I_{x_0}.$$

En vertu du corollaire de la condition A pour chaque $z \in R$ et $y \in I_{x_0}$ on a $zy \in I_{x_0}$; d'une manière analogue $yz \in I_{x_0}$, c'est-à-dire $I_{x_0}$ est un idéal bilateral. Il n'est pas trivial parce que $e \overline{\in} I_{x_0}$, car dans le cas contraire on aurait $e < tx_0$, ce qui contredit à ce que $x_0$ est un élément frontière. Ce que $I_{x_0}$ est un idéal fondamental, est évident.

Théorème I. *Si la condition* A *est remplie dans* $R$ *et s'il existe des éléments qui diffèrent de* $\lambda e$ ($\lambda$ *étant un nombre réel*), *alors* $R$ *contient un idéal fondamental.*

Si $R$ contient des éléments $y \neq 0$, pour lesquels $\inf t = 0$ ($-te < y < te$), il est facile à montrer que l'ensemble de tous les éléments de cette nature forme un idéal fondamental. S'il n'existe pas de tels éléments, alors dans $R$ on a la condition B. Introduisons dans $R$ une nouvelle loi pour semi-ordonner: considérons comme positifs tous les éléments $x > 0$ et les éléments $y$ de la forme $\rho_x e - x$. Alors il est facile à voir que pour cette nouvelle loi dans $R$ les axiomes I—IV et la condition C seront remplis. En vertu des remarques I et II il existe dans $R$ un idéal fondamental au sens de la nouvelle loi pour semi-ordonner, mais alors il sera aussi fondamental dans le sens précédent. Le théorème est démontré.

Corollaire. *Un corps semi-ordonné vérifiant les axiomes* I—IV *et la condition* A *est en similitude isomorphe avec l'ensemble des nombres réels.*

2. Soit $I$ un idéal fondamental de l'anneau. Considérons l'anneau des résidus $R/I$.

Lemme I. *Si* $R$ *est un anneau semi-ordonné, où la condition* A *est remplie, alors l'anneau des résidus* $R/I$ *par rapport à l'idéal fondamental peut être fait semi-ordonné de telle manière que les axiomes* I—IV *et la condition* A *y soient remplis.*

Écrivons $X > 0 (X \in R/I)$, si $X \neq I$ et si $X$ contient un élément $x > 0$ ($x \in R$). Il est facile à vérifier que dans ces conditions les axiomes I, III, IV et la condition A sont remplis. Montrons que l'axiome II est aussi vrai. Soit $X > 0$ et $Y > 0$, c'est-à-dire il existe des $x$, $y > 0$ tels que $x \in X$ et $y \in Y$. Alors l'élément $x + y > 0$ appartient à $X + Y$. Il reste à démontrer que $X + Y \neq I$. Mais dans le cas contraire $x + y \in I$, et comme $I$ est fondamental et $0 < x < x + y$, on a $x \in I$, ce qui contredit à $X \neq I$. Le lemme est démontré.

Comme d'habitude, on démontre par induction transfinie que chaque idéal fondamental est contenu dans un idéal fondamental maximum, c'est-à-dire dans l'idéal fondamental qui n'est contenu dans aucun autre.

Théorème II. *Soit $R$ un anneau semi-ordonné, vérifiant la condition* A, *$M$ — un idéal fondamental maximum de $R$. Alors l'anneau semi-ordonné des résidus $R/M$ est en similitude isomorphe avec le corps des nombres réels.*

D'après le lemme I la condition A est remplie dans $R/M$. Supposons que $R/M$ contient un élément $X \neq \lambda\varepsilon$; alors, en vertu du théorème I, il contient un idéal fondamental $\mathfrak{A}$. En prenant la somme de toutes les classes appartenant à $\mathfrak{A}$, nous obtiendrons un idéal fondamental de $R$ contenant $M$, ce qui est en contradiction avec le fait que $M$ est maximum. Ainsi à chaque $x \in R$ et à l'idéal maximum $M$ il correspond un nombre réel que nous désignerons par $x(M)$.

Désignons par $\mathfrak{M}$ l'ensemble de tous les idéaux maximum de l'anneau $R$. A chaque $x \in R$ faisons correspondre une fonction définie sur $\mathfrak{M}$ $x \longrightarrow x(M)$ $(M \in \mathfrak{M})$.

La correspondance obtenue est une représentation homomorphe de l'anneau $R$ sur l'anneau des fonctions bornées sur $\mathfrak{M}$, et d'ailleurs, si

$$x > 0, \text{ alors } x(M) \geqslant 0 \quad (M \in \mathfrak{M}). \tag{1}$$

D'ailleurs, l'idéal $I_0$ sera le noyau de homomorphie dont on a parlé dans la démonstration du théorème I. Il en résulte que si la condition B est remplie dans $R$, notre homomorphie devient un isomorphisme.

Enfin, si la condition C est remplie dans $R$, cette correspondance isomorphe jouit des propriétés: si $x > 0$, alors $x(M) \geqslant 0$, et inversement, c'est-à-dire l'anneau est en similitude isomorphe avec un sous-anneau de l'anneau des fonctions réelles bornées sur $\mathfrak{M}$.

En effet, la première partie est vraie même dans la condition A. Soit maintenant $x \in R$ non positif. Alors $\rho_{-x} \neq 0$ et l'élément $x_0' = \rho_{-x} e + x$ sera un élément frontière. En vertu de la remarque II, l'élément $x_0'$ appartient à l'idéal fondamental $I_{x_0'}$, donc à un certain idéal fondamental maximum $M_0$. Mais alors on a évidemment $x(M_0) = -\rho_{-x} < 0$, c. q. f. d.

3. Introduisons dans $\mathfrak{M}$ une topologie faible au moyen d'un système déterminant de voisinages $U(M_0, x_1, \ldots, x_n, \varepsilon)$ $[M_0 \in \mathfrak{M};\ x_1, \ldots, x_n \in R;\ \varepsilon > 0;\ n = 1, 2, \ldots]$, où $U(M_0, x_1, \ldots, x_n, \varepsilon)$ est l'ensemble de tous les $M \in \mathfrak{M}$, pour lesquels $|x_k(M) - x_k(M_0)| < \varepsilon$ pour tous les $k = 1, 2, \ldots, n$.

Dans cette topologie $\mathfrak{M}$ sera un bicompact (c'est-à-dire un espace bicompact de Hausdorff) et les fonctions $x(M)$ — des fonctions continues sur $\mathfrak{M}$. En tenant compte d'un résultat de Stone [3], nous aurons le.

Théorème IV. *Un anneau semi-ordonné $R$ vérifiant la condition* C *est en similitude isomorphe avec un sous-anneau de l'anneau de toutes les fonctions continues, définies sur un certain bicompact, dense dans tout l'anneau.*

Enfin, indiquons que les résultats de cet article permettent de faire quelques conclusions sur la réalité des anneaux normés vérifiant la condition que $x_1^2 + x_2^2 + \ldots + x_n^2 \neq 0$ pour tous les $x_k \in R$ et $n = 1, 2, \ldots$.

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*PHYSIK*

# AKTIVIERENDE WIRKUNG DES SICHTBAREN LICHTES AUF DIE ULTRAVIOLETTE LUMINESZENZ VON ALKALIHALOGENIDKRISTALLEN

Von M. L. KATZ

*(Vorgelegt von S. I. Wawilow, Mitglied der Akademie, den 16. I. 1941)*

Den modernen theoretischen Vorstellungen gemäss sind verschiedene Mechanismen der Bildung metastabiler Elektronenzustände in Kristallen von Alkalihalogenidverbindungen möglich. So betrachten de Boer ([1]) und Mott ([2]) die *F*-Zentren als Elektronen, die um positive, durch das Fehlen von negativen Ionen des Gitters entstandene, «Löcher» lokalisiert sind. Lokalisierte Zustände können auch durch fremde Ionen oder andere Fremdkörper, sowie auch durch innere kleine Risse erzeugt werden, die zur Bildung der von Tamm ([3]) erstmals erwähnten Flächenniveaus führen.

Eine Lokalisierung des Elektrons kann auch bei Fehlen im Kristalle jeglicher Strukturdefekte stattfinden. In diesem Falle findet sie entweder infolge der Zerstreuung der Energie durch das erregte Elektron und des damit verbundenen Umbaus des Gitters ([4]), oder wegen der, durch den Erregungszustand bedingten Deformation, statt ([5]). Die erwähnten Energiezustände werden auch mit den *F*-Zentren in Alkalihalogenidkristallen identifiziert ([4,6]). Somit ist es zu erwarten, dass diese Zustände sich nach der Verbindungsenergie des Elektrons im lokalisierten Zustande voneinander unterscheiden können je nachdem, durch welchen von den obenangeführten Mechanismen sie gebildet werden. Diese Erscheinungen können im Abbauprozess der Lokalisationszustände auftreten.

Aus diesem Beweggrund habe ich eine Untersuchung der ultravioletten Lumineszenz photochemisch verfärbter Alkalihalogenidkristalle, die die Prozesse optischer und thermischer Dissoziation der *F*-Zentren begleitet, unternommen.

Die Untersuchungen wurden an natürlichen NaCl-Monokristallen und künstlichen, sorgfältig von Beimengungen gereinigten, KCl-Monokristallen, die aus einer Schmelzung nach Kyropoulos erzeugt wurden, durchgeführt. Die Messungen wurden vermittelst eines höchstempfindlichen Lichtzählrohrs mit einer sensibilisierten Platinphotokathode ausgeführt. Zur Spektralerforschung der Lumineszenz diente ein Leiss-Monochromator mit Quarzoptik. Zur Aktivierung der Lumineszenz durch monochromatisches sichtbares Licht wurde ein Zeiss-Monochromator mit Glassoptik verwendet. Die Phosphoreszenz der NaCl- und KCl-Kristalle wurde durch monochromatisches Licht einer kondensierten Al-Funkenentladung folgender Wellenlänge erregt: $\lambda=1935$ Å und $\lambda=1989$ Å. Die erhaltenen Resultate sind folgende.

1. Die Abklingung der die Abbauprozesse der *F*-Zentren begleitenden ultravioletten Phosphoreszenz von NaCl- und KCl-Monokristallen verläuft nach dem Exponentialgesetz.

Die Kurve *a* in Abb. 1 stellt den zeitlichen Verlauf der Zahl der im Lichtzählrohr durch Phosphoreszenz des NaCl-Kristalls hervorgerufenen Impulse dar. Die Kurve *a'* der Abb. 2 zeigt den zeitlichen Verlauf des Logarithmus der Impulszahl der Kurve. Wie aus den Abbildungen ersichtlich, entsprechen die Kurven einer einfachen Exponentialfunktion. Die Konstante der Abklingungszeit beträgt für NaCl $1.35\times10^3$ Sek., und für KCl $1.27\times10^3$ Sek.

In plastisch deformierten NaCl-Kristallen wird eine Abweichung von dem Exponentialgesetz der Abklingung beobachtet, welche durch Anwesenheit von zwei Spektralbanden mit verschiedener Abklingungszeit herforgerufen wird (7). Die in dieser Arbeit angeführten Ergebnisse wurden an Kristallen, die keiner speziellen plastischen Deformation unterworfen wurden, erhalten.

2. Die Beleuchtung des Kristalls mit sichtbarem monochromatischem Licht im Moment, wo seine ultraviolette Phosphoreszenz praktisch einge-

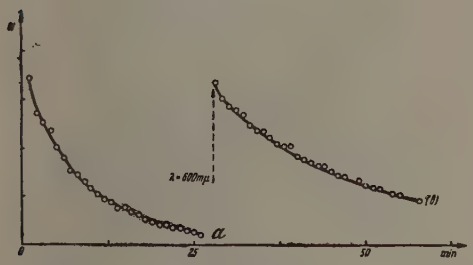


Abb. 1.

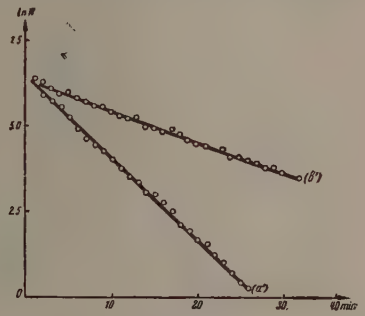


Abb. 2.

stellt ist, erzeugt ein ultraviolettes Leuchten, dessen Intensität von der Intensität des erregenden sichtbaren monochromatischen Lichtes abhängig ist.

Die Kurven *a* und *b* geben ein vollständiges Bild der beobachteten Erscheinung. Die Kurve *a* ist bereits erwähnt worden. Die Kurve *b* zeigt eine zeitliche Intensitätsveränderung des ultravioletten KCl-Leuchtens bei kontinuierlicher Beleuchtung des Kristalls mit sichtbarem monochromatischem Licht $\lambda=600$ mμ, das nach praktisch völligem Einstellen der Phosphoreszenz des Kristalls eingeschaltet wird. In Abb. 2 stellt die Kurve *b'* die Veränderung des Logarithmus der Zahl der Impulse *N* der Kurve *b* der Abb. 1 in Abhängigkeit von der Zeit dar. Aus den Abbildungen ist ersichtlich, dass die Intensität des ultravioletten Leuchtens eines verfärbten Kristalls, der durch monochromatisches Licht $\lambda=600$ mμ nach praktisch völligem Einstellen seiner Phosphoreszenz erregt wird, auch nach dem Exponentialgesetz nachlässt. Die Konstante der Abklingungszeit $\tau=3.25\times10^3$ Sek. ist in diesem Falle grösser als im vorhergehenden. Die Leuchtintensität, bei kontinuierlicher Beleuchtung des Kristalls mit sichtbarem monochromatischem Lichte, nimmt in allen Fällen nach dem Exponentialgesetz ab, aber der Neigungswinkel der Geraden hängt von der Wellenlänge des sichtbaren Lichtes ab. So ist bei $\lambda=450$ mμ $\tau=1.42\times10^4$ Sek.

3. Es wird keine analoge Wirkung des sichtbaren Lichtes auf die ultraviolette Lumineszenz von durch Thallium aktivierten Alkalihalogenidphosphoren (KCl+0.23 Mol. % TlCl und Nacl+0.34 Mol. % TlCl) beobachtet. Die Beleuchtung des Kristalls KCl+TlCl mit sichtbarem monochromatischem Lichte erzeugt kein ultraviolettes Leuchten, nach völligem Einstellen seiner Phosphoreszenz, wie im Falle von Alkalihalogenidkristallen ohne Beimengung von Thallium. Dies scheint zu bezeugen, dass das Leuchten der durch Tl aktivierten KCl- und NaCl-Kristalle durch eine Art Zentren bedingt

ist, welche in den normalen Zustand auch ohne optische Aktivierung übergehen. Das sichtbare Licht vergrössert nur die Übergangswahrscheinlichkeit. So vergrössert die Beleuchtung des KCl+TlCl-Kristalls mit sichtbarem monochromatischem Lichte die Emissionsgeschwindigkeit der Lichtsumme für alle Wellenlängen des sichtbaren Lichtes.

4. Die Kurven der Spektralverteilung der aktivierenden Wirkung des sichtbaren Lichtes auf die Lumineszenz verfärbter KCl- und NaCl-Kristalle, auf gleiche Energien des auf den Kristall fallenden Lichtes bezogen, zeigen keinen wesentlichen Unterschied von den Absorptionsspektralkurven dieser Kristalle in der *F*-Bande. Dieses Zusammentreffen weist auf eine direkte Verbindung, die zwischen dem Dissoziationsprozess der *F*-Zentren und der ultravioletten Lumineszenz des Kristalls besteht, hin.

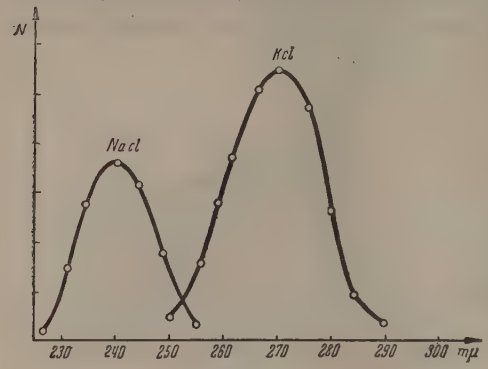

Abb. 3.

5. Das Spektrum der ultravioletten Phosphoreszenz von KCl-Monokristallen besteht im Intervalle von 2000 Å bis 3150 Å aus einer Bande mit einem Maximum bei $\lambda=270$ mμ. Das Phosphoreszenzspektrum von plastisch undeformierten NaCl-Kristallen besteht auch im erwähnten Intervall aus einem Bande mit einem Maximum bei etwa $\lambda=400$ mμ.

Die Leuchtungsspektren verfärbter KCl- und NaCl-Kristalle, die durch monochromatisches sichtbares Licht nach Einstellen der Phosphoreszenz erregt werden, sind den Phosphoreszenzspektren dieser Kristalle analog (Abb. 3). Ein Erwärmen des Kristalls (125°C) nach völligem Einstellen seiner Phosphoreszenz erzeugt ebenso ein ultraviolettes Leuchten von einem analogen Spektralbestand.

Somit ist die Lumineszenz von alkalihalogeniden KCl- und NaCl-Kristallen, die den Abbauprozess der *F*-Zentren begleitet, durch zwei Arten von Zentren bedingt: die Zentren der einen Art (Kurve *a* der Abb. 1) gehen aus dem erregten in den normalen Zustand ohne Einwirkung von Aussenfaktoren über, während die Zentren der zweiten Art (Kurve *b* der Abb. 1), unter den übrigen gleichen Bedingungen, in den normalen Zustand nur unter Einwirkung einer optischen oder thermischen Aktivierung übergehen.

Die Identität der Leuchtungsspektren, durch obenerwähnte Zentren bedingt, scheint zu bezeugen, dass der Übergang der Elektronen auf ein und dasselbe Energieniveau erfolgt, und somit unterscheiden sich die Zentren voneinander nur nach ihrer Aktivierungsenergie.

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*PHYSICS*

# INTENSITIES OF VIBRATIONAL SPECTRA OF MOLECULES

By M. W. WOLKENSTEIN

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The modern theory fails to account for the distribution of intensities in the Raman and infra-red spectra of molecules. The same can be said of the state of polarisation of Raman lines. Placzeck's theory gives the values of the degree of depolarisation for special cases only (1). We suggest a semiempirical method of calculation of the intensities and of the depolarisation degree suitable for any molecules. This method is based on the conception of vectorial and tensorial additivity. The addition of the polarisability ellipsoids was applied by Stuart and Volkmann (2) and by Otterbein (3) in their investigations of the Kerr effect. Placzeck has pointed out the possibility of applying these ideas to our purposes (4).

Let us investigate as an example the triatomic symmetrical non-linear molecule with the valence angle $2\gamma$ and with the masses $m$, $M$ and $m$. The components of polarisability of the first and second valence linkage will be denoted by $\alpha_{11}, \alpha_{12}, \alpha_{13}$ and $\alpha_{21}, \alpha_{22}, \alpha_{23}$, respectively; in the general case ($\pi$-bonds) the ellipsoid must be triaxial. In the equilibrium state we have $\alpha_{11}=\alpha_{21}=\alpha_1$, $\alpha_{12}=\alpha_{22}=\alpha_2$ and $\alpha_{23}=\alpha_{33}=\alpha_3$. The potential energy of a molecule in the electrical field is the sum of the energies of separate linkages. The principal axes of polarisability can be found in our case from a simple consideration of symmetry and in general can be found by transforming the potential energy into the canonical form. We obtain:

$$-2U = a_1 E_x^2 + a_2 E_y^2 + a_3 E_z^2 \qquad (1)$$

where

$$a_1 = 2(\alpha_1 \sin^2\gamma + \alpha_2 \cos^2\gamma); \quad a_2 = 2(\alpha_1 \cos^2\gamma + \alpha_2 \sin^2\gamma); \quad a_3 = 2\alpha_3. \qquad (2)$$

The $Y$-axis is a bisector of the valence angle, $X$-axis lies in the plane of the molecule.

During the vibrations in this plane the symmetry will be disturbed in the general case and we obtain for the same axes:

$$-2U = b_1 E_x^2 + 2b_{12} E_x E_y + b_2 E_y^2 + b_3 E_z^2 \qquad (3)$$

where

$$\left.\begin{aligned} b_1 &= \alpha_{11}\sin^2\gamma + \alpha_{12}\cos^2\gamma + \alpha_{21}\sin\gamma + \alpha_{22}\cos^2\gamma \\ b_{12} &= (\alpha_{11} - \alpha_{12} + \alpha_{22} - \alpha_{21})\sin\gamma\cos\gamma \\ b_2 &= \alpha_{11}\cos^2\gamma + \alpha_{12}\sin^2\gamma + \alpha_{21}\cos^2\gamma + \alpha_{22}\sin^2\gamma \\ b_3 &= \alpha_{13} + \alpha_{23} \end{aligned}\right\} \qquad (4)$$

The electrical moments induced in the vibrating molecule are equal to [5]:

$$\left.\begin{aligned}
\mu_{xi} &= -\frac{\partial U}{\partial E_x} = \left[b_{10} + \left(\frac{\partial b_1}{\partial Q_i}\right)_0 Q_{io}\right] E_x + \left(\frac{\partial b_{12}}{\partial Q_i}\right)_0 Q_{io} E_y + \left(\frac{\partial b_{13}}{\partial Q_i}\right)_0 Q_{io} E_z \\
\mu_{yi} &= -\frac{\partial U}{\partial E_y} = \left(\frac{\partial b_{12}}{\partial Q_i}\right)_0 Q_{io} E_x + \left[b_{20} + \left(\frac{\partial b_2}{\partial Q_i}\right)_0 Q_{io}\right] E_y + \left(\frac{\partial b_{23}}{\partial Q_i}\right)_0 Q_{io} E_z \\
\mu_{zi} &= -\frac{\partial U}{\partial E_z} = \left(\frac{\partial b_{13}}{\partial Q_i}\right)_0 Q_{io} E_x + \left(\frac{\partial b_{23}}{\partial Q_i}\right)_0 Q_{io} E_y + \left[b_{30} + \left(\frac{\partial b_3}{\partial Q_i}\right)_0 Q_{io}\right] E_z
\end{aligned}\right\} \quad (5)$$

$Q_i$ is a normal co-ordinate of the vibration $i$. The intensities and the degrees of depolarisation of Raman lines are determined by the mean value and anisotropy of the tensor $\left(\frac{\partial b_{kj}}{\partial Q_i}\right)_0 Q_{io}$. We can find the derivatives in the following way:

$$\left(\frac{\partial b_{kj}}{\partial Q_i}\right)_0 = \sum_n \left(\frac{\partial b_{kj}}{\partial q_n}\right)_0 \left(\frac{\partial q_n}{\partial Q_i}\right)_0 \quad (6)$$

where $q_n$ are the changes in lengthes of the valence linkages and of the valence angles (by using the valence-force model). The derivatives $\left(\frac{\partial q_n}{\partial Q_i}\right)_0$ can be taken from the equations of motion. We can write the mechanical potential energy in our case in the following form

$$U' = \frac{1}{2} k (q_1^2 + q_2^2) + \frac{1}{2} c q_3^2 \quad (7)$$

where $q_1$ and $q_2$ are the changes in lengthes of linkages $m - M$, and $q_3$ the change in the valence angle. From the equations of motion * we obtain

$$q_1 + q_2 = C_1 Q_1 + C_2 Q_2; \quad q_3 = -C_1 D_1 Q_1 - C_2 D_2 Q_2; \quad q_1 - q_2 = C_3 Q_3 \quad (8)$$

where

$$D_{1,2} = \frac{\omega_{1,2}^2 - \frac{k}{m}\left(1 + \frac{2m}{M}\cos^2\gamma\right)}{2\frac{\sin 2\gamma}{Ms} c} \quad (9)$$

$s$ is the length of the linkage $m - M$ in equilibrium state. We find the coefficients $C_1$ by the normalisation

$$C_{1,2}^2 = \frac{\omega_{1,2}^2}{\frac{k}{2} + c D_{1,2}^2}; \quad C_3^2 = \frac{2\omega_3^2}{k}. \quad (10)$$

Using the equations (4) and (8) we obtain the following expressions for the mean values and anisotropies of the tensor $\left(\frac{\partial b_{kj}}{\partial Q_i}\right)_0$ for all normal vibrations:

$$\left.\begin{aligned}
\beta_{1,2} &= \frac{C_{1,2}}{3}\left(\frac{\partial \alpha_1}{\partial r} + \frac{\partial \alpha_2}{\partial r} + \frac{\partial \alpha_3}{\partial r}\right)_0 \\
\gamma_{1,2}^2 &= \frac{C_{1,2}^2}{2}\left\{\left[\left(\frac{\partial \alpha_1}{\partial r} - \frac{\partial \alpha_2}{\partial r}\right)_0 (\sin^2\gamma - \cos^2\gamma) - 4 D_{1,2} (\alpha_1 - \alpha_2) \sin 2\gamma\right]^2 + \right. \\
&\quad + \left[\left(\frac{\partial \alpha_1}{\partial r}\sin^2\gamma + \frac{\partial \alpha_2}{\partial r}\cos^2\gamma - \frac{\partial \alpha_3}{\partial r}\right)_0 - 2 D_{1,2} (\alpha_1 - \alpha_2) \sin 2\gamma\right]^2 + \\
&\quad \left. + \left[\left(\frac{\partial \alpha_1}{\partial r}\cos^2\gamma + \frac{\partial \alpha_2}{\partial r}\sin^2\gamma - \frac{\partial \alpha_3}{\partial r}\right)_0 + 2 D_{1,2} (\alpha_1 - \alpha_2) \sin 2\gamma\right]^2\right\} \\
\beta_3 &= 0; \quad \gamma_3^2 = \frac{3}{4} C_3^2 \left(\frac{\partial \alpha_1}{\partial r} - \frac{\partial \alpha_2}{\partial r}\right)_0^2 \sin^2 2\gamma
\end{aligned}\right\} \quad (11)$$

* See, for instance, the article by Eliashevich [6].

Thus, we have expressed all the necessary quantities by means of $\alpha$ and $\frac{\partial\alpha}{\partial r}$ of the separate linkages. It is quite clear that the symmetry relations being undisturbed, we obtain automatically all Placzeck's selection rules. We see, for instance, that the vibration $Q_3$ has $\rho=\frac{6}{7}$ and is forbidden for the linear symmetrical triatomic molecule as $\sin 2\gamma=0$.

There exists no theory for calculating $\frac{\partial\alpha}{\partial r}$. The conception of Silberstein (7) leads to quite erroneous results in this case. The most reasonable way is the semiempirical one. We can use the values $\frac{\partial\alpha}{\partial r}$ and $\alpha$ evaluated from experiment to calculate other data. We applied this method to the molecule of dichloromethane $CH_2Cl_2$. The following experimental data are available in this case: $\omega_1=285$ cm$^{-1}$, $\omega_2=700$ cm$^{-1}$, $\omega_3=736$ cm$^{-1}$, $2\gamma=108°$, $s=1.8$ Å. From this we have $k=2.65\times10^5$ dyne/cm, $C=0.54\times4\times10^5$ dyne/cm$^2$. The calculation gives: $D_1=-0.32\times10^8$ cm$^{-1}$, $D_2=0.16\times10^8$ cm$^{-1}$, $C_1^2=0.023$, $C_2^2=0.199$, $C_3^2=0.242$. The Kerr effect gives for the C—Cl linkage: $\alpha_1=3.37\times10^{-24}$ cm$^3$, $\alpha_2=\alpha_3=2.21\times10^{-24}$ cm$^3$. We need two equations for determining $\left(\frac{\partial\alpha_1}{\partial r}+2\frac{\partial\alpha_2}{\partial r}\right)_0$ and $\left(\frac{\partial\alpha_1}{\partial r}-\frac{\partial\alpha_2}{\partial r}\right)_0$. Using the value $\rho=0.2$ for the Raman line of C—Cl in the molecule $CH_3Cl$, we obtain the first equation:

$$0.2=\frac{6\left(\frac{\partial\alpha_1}{\partial r}+\frac{\partial\alpha_2}{\partial r}\right)_0^2}{5\left(\frac{\partial\alpha_1}{\partial r}+2\frac{\partial\alpha_2}{\partial r}\right)_0^2+7\left(\frac{\partial\alpha_1}{\partial r}-\frac{\partial\alpha_2}{\partial r}\right)_0^2}. \tag{12}$$

The second equation can be taken for $\rho_1=0.25$ of the frequency 285 cm$^{-1}$ (10) for dichloromethane. Consequently

$$\left.\begin{aligned}\gamma'&=\left(\frac{\partial\alpha_1}{\partial r}-\frac{\partial\alpha_2}{\partial r}\right)_0=1.54\times10^{-16}\ \text{cm}^2\\ \beta'^2&=\left(\frac{\partial\alpha_1}{\partial r}+2\frac{\partial\alpha_2}{\partial r}\right)_0=11\times10^{-32}\ \text{cm}^4\end{aligned}\right\} \tag{13}$$

or the second pair of solutions of the quadratic equation:

$$\gamma'=-0.32\times10^{-16}\ \text{cm}^2,\quad \beta'^2=3.3\times10^{-32}\ \text{cm}^4. \tag{13a}$$

We calculate $\rho_2$ for $\omega_2=700$ cm$^{-1}$, using the first pair of values (13): $\rho_2=0.06$. The experimental value is $\rho_2=0.07$.

Inversely, the calculation of $\rho_1$ by using $\rho_2$ gives $\rho_1=0.29$ instead of $\rho_1=0.25$ and the two pairs of solutions

$$\gamma'=1.3\times10^{-16}\ \text{cm}^2,\qquad \beta'^2=7.8\times10^{-32}\ \text{cm}^4 \tag{13b}$$

$$\gamma'=13.3\times10^{-16}\ \text{cm}^2,\qquad \beta'^2=815\times10^{-32}\ \text{cm}^4. \tag{13c}$$

The first pairs (13) and (13b) in both cases are in good concordance and the values are more verisimilar. The second pairs (13a) and (13c) are evidently not physical solutions. We can determine the values $\left(\frac{\partial\alpha}{\partial r}\right)_0$. Using the values (13) we obtain

$$\left(\frac{\partial\alpha_1}{\partial r}\right)_0=-0.1\times10^{-16}\ \text{cm}^2,\ \left(\frac{\partial\alpha_2}{\partial r}\right)_0=-1.6\times10^{-16}\ \text{cm}^2$$

or

$$\left(\frac{\partial\alpha_1}{\partial r}\right)_0=2.1\times10^{-16}\ \text{cm}^2,\qquad \left(\frac{\partial\alpha_2}{\partial r}\right)_0=0.6\times10^{-16}\ \text{cm}^2.$$

Additional considerations will probably allow us to remove this ambiguity.

Using the calculated values of $\beta'^2$ and $\gamma'$, we obtain the intensities of the three Raman lines of dichloromethane by the equation*

$$J(\omega - \omega_i) \sim J_p \cdot \frac{C_i^2}{\lambda^{14}} (5\beta_i'^2 + 13\gamma_i'^2) \frac{Q_{i0}^2}{1 - e^{-\frac{h\nu_i}{kT}}} \qquad (14)$$

where

$$Q_{i0}^2 = \frac{h}{8\pi^2\nu_i}.$$

In the following table the calculated and observed data are compared (the intensity of the line 700 $cm^{-1}$ is always taken as 10).

| | Calculated | Experimental(8) (evaluated by sight) | Experimental (10) (evaluated by sight) |
|---|---|---|---|
| $\omega_1$ | 5.9 | 8.3 | 3.3 |
| $\omega_2$ | 10 | 10 | 10 |
| $\omega_3$ | 3.8 | 5 | 2 |

In this way we obtain a good qualitative agreement. The order of distribution of intensities is reproduced correctly.

The calculation of intensities in infra-red spectra can be deduced from the same notions. We need here the values $\left(\frac{\partial \mu_i}{\partial Q_i}\right)_0 Q_{i0}$. In the case of a triatomic symmetrical non-linear molecule we have the following relations ($\mu_1$ and $\mu_2$ are the dipole moments of two $m-M$ bonds):

$$\mu_x = \mu_1 \sin\gamma - \mu_2 \sin\gamma, \quad \mu_y = \mu_1 \cos\gamma + \mu_2 \cos\gamma, \quad \mu_z = 0 \qquad (15)$$

$$\left.\begin{aligned} \left(\frac{\partial \mu_x}{\partial Q_{1,2}}\right)_0 = 0, \quad \left(\frac{\partial \mu_y}{\partial Q_{1,2}}\right)_0 = C_{1,2}\left(\frac{\partial \mu}{\partial r}\cos\gamma + 2D_{1,2}\mu \sin\gamma\right) \\ \left(\frac{\partial \mu_x}{\partial Q_3}\right)_0 = C_3 \frac{\partial \mu}{\partial r}\sin\gamma, \quad \left(\frac{\partial \mu_y}{\partial Q_3}\right)_0 = 0. \end{aligned}\right\} \qquad (16)$$

The further calculation is not complicated.

The considerations developed above make it possible to determine the intensities in infra-red Raman spectra and the degrees of depolarisation of Raman lines by using the data from the Kerr effect, interatomic distances and numeric values of frequencies. The method proposed above permits to solve some problems which received no solution in the theory of Placzeck. It makes it possible to determine $\left(\frac{\partial \alpha}{\partial r}\right)_0$ and $\left(\frac{\partial \mu}{\partial r}\right)_0$ from the relations between the intensities of lines in vibrational spectra.

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* Placzeck [11] has erroneously omitted in his formula the factor $Q_{i0}^2$.

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*PHYSICS*

# ELECTRONOGRAPHIC DETERMINATION OF THE IDENTITY PERIOD *C*

By Z. G. PINSKER

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Electronography has been successfully applied of late to the solution of problems of structural analysis, but the electronographic structural analysis as an independent method is not yet sufficiently developed. This is true, in particular, of the determination of dimensions of a unit cell. In the case of complicated space lattices, possessing a rather distinct cleavage which is usually referred to the plane (001) of the crystal (the basal plane), and there is a vast number of such space lattices among all types of compounds, the electronographic method often encounters difficulties in determining the length of the unit cell perpendicular to the basis, i. e. along the axis $C$. An important reservation should be made at the very outset: in a number of instances investigators instead of determining the length of the unit cell along $C$ merely check the value which was previously suggested with the given space-lattice pattern. This checking is, naturally, of limited importance and is characterized, particularly, by a non-univocal solution, like in the determination of structure from powder photographs. In contrast to this in the present paper is discussed an independent method of measuring the identity period along the axis $C$, which is similar to that employed in the case of rotation photographs.

Various substances, both soluble (halides of heavy metals, organic crystals, etc.) and insoluble (complex minerals and, in particular, large groups of silicates), often give grounds for referring them to the so-called two-dimensional crystals, when very thin specimens, required for purpose of electronography, are prepared out of these substances. The structure of these remarkable compounds is generally described as a «two-dimensional molecule», i. e. their composition in a very thin section, from 2 to 8—10 atom layers in thickness, corresponds to their chemical formula multiplied, of course, by a sufficiently large number $n$. These layers are highly tenacious. As far as cohesion of separate layers is concerned, a regular pattern along the axis $C$ is distorted in many instances and, especially, in electronographic specimens, this distortion being the result of an extremely weak linkage. Separate sheets, consisting of a few «molecular layers», referred to above, become displaced in different directions with respect to each other, and this also deteriorates the diffraction effect in the direction $C$. A small resolving power along $C$ axis is, however, the usual cause of diffraction effect complications in such thin films.

The pronounced cleavage of these lattices along the basis results in a more or less exact orientation of the crystal planes (001) || to the film; such an orientation is always observed in thin films. If, moreover, a strict azimuthal orientation has remained undistorted, such films give characteristic monocrystal photographs which may be used for an exact and independent determination of the identity period in the basal plane. With these quantities known and reflexions in the basal plane indexed, it is possible to proceed to the determination of the length of $C$ for the unit cell, this being in essence the subject of the present paper. Films with a disorderly azimuthal setting of crystals suit this purpose better than monocrystal films, as the former, in a position $\perp$ to the electron beam, yield the pattern consisting of a few regularly shaped Debye rings which correspond to prismatic planes only. If the specimen is turned about the axis lying in its plane, it leaves the position in which the texture axis and the electron beam coincide, and as a result there appears the characteristic pattern, first discovered by Kirchner for $CdI_2$ films. Circles due to prismatic planes degenerate into arcs lying on a straight line || to the axis of rotation of the specimen. On the other hand, there simultaneously appear arcs corresponding to pyramidal planes; the latter arcs are located on ellipses whose major axes are $\perp$ to the axis of rotation of the specimen and which are often traced by weaker lines. It should be pointed out, however, that this pattern cannot be examined in detail nor measured and used for calculations, unless a sufficiently powerful apparatus is available. In an electronograph of the usual type with the distance of $\sim$ 300 mm from the specimen to the photographic plate, there occurs an overlapping of arcs and the ellipses are outlined by wide diffuse bands which are especially noticeable at the ends of the major axis. In order to calculate the values of $C$ from the electronogram thus obtained, the mechanism of its formation should first be examined, and the reciprocal lattice may serve this purpose. It is obvious that by means of the reciprocal lattice an image of our specimen, with the texture axis $\perp$ to the film, may be received, if all points of the reciprocal lattice are rotated about the axis $C^*$(i. e. about the axis $C$ in the reciprocal lattice). Points with the same value of $1/d^2$ will give circles, and a series of circles of the same radius will correspond to equal $h, k$ indices and to a successive range $l$ of values from $-p$ to $+p$, where $p=1,2,3..$. Let us refer to Fig. 1. The Ewald sphere which degenerates here into the plane $N$, perpendicular to a new direction of the electron beam, forms an angle $\theta$ with the plane of circles of the reciprocal lattice. When the plane $N$ intersects the circles mentioned above, an interference image, consisting of pairs of points, is obtained; points of the reciprocal lattice with the same values of $l$ and possessing indices $h+1$, $k$ or $h$, $k+1$, etc. give a set of circles concentric to those shown in Fig. 1. On intersecting with the plane $N$ these circles give new points arranged in rows along the layer lines of the type $PQ$ || to the axis $Y$. The construction performed in Fig. 1 refers to the case of exact texture. As a matter of fact, the basal planes of the crystals form finite angles with the film plane; this corresponds in the reciprocal lattice to the fitting of the axis $C$ and with it of the planes of the circles. The latter form spherical layers which on intersecting with the plane $N$ produce arcs. Therefore, an electronographic pattern is made up not of spots, but of more or less short arcs lying along the ellipse. In the case of a simultaneous participation of comparatively thick and very thin crystals in diffraction (due to passing of a wide beam through the film), the thin crystals may bring about a superimposition of continuous ellipses on the pattern described above. In Fig. 1 is shown, indeed, a series of separate circles; thin films having an insignificant resolution along the axis $C$ will give in the reciprocal lattice a practically continuous cylindrical surface which, being intersected by the

plane $N$, gives an ellipse. A closer examination of Fig. 1 makes possible the deduction of all formulae needed for the determination of $C$. The small shaded triangle gives, indeed, the relation of the distance between layer lines on the plane $N$ to the value $C^*$:

$$C^* = h \sin \theta. \qquad (1)$$

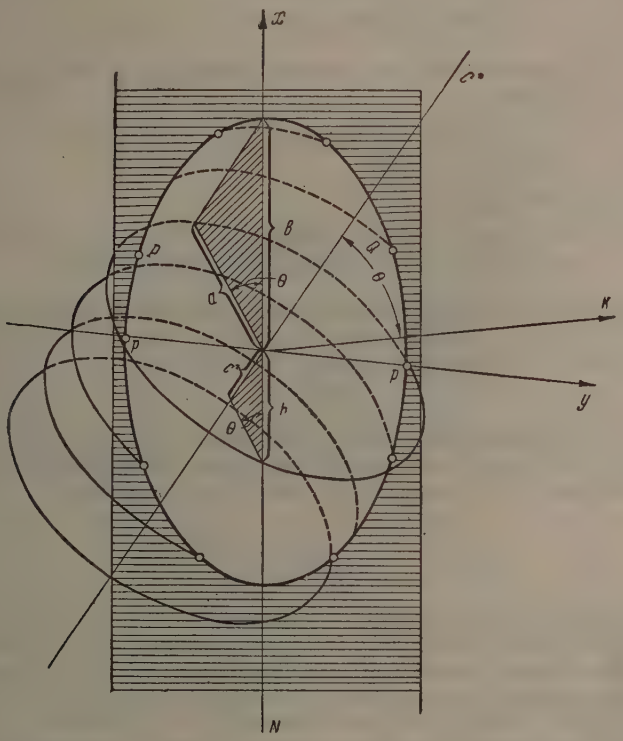


Fig. 1.

Substituting $1/C$ for $C^*$ and introducing the scale $D\lambda$ for the transition from the reciprocal lattice to the electronogram, we obtain

$$C = \frac{D\lambda}{h \sin \theta}. \qquad (2)$$

The angle $\theta$ is determined from the ratio of semiaxes of the ellipse. The large shaded triangle in Fig. 1 gives directly

$$\frac{a}{b} = \cos \theta. \qquad (3)$$

The equations thus obtained may be transformed into expressions which are more convenient for practical purposes. The greatest accuracy in determining the value of $h$ is achieved, in fact, when taking photographs under large angles, as more layer lines are thus formed on the electronogram. But the direct measurement of its length is possible only for one of the two ellipses, this being due to elongation of the ellipses in the direction of the axis $2a$. Moreover, ends of the major axes are not marked, in general, by reflections. Measuring the distance $2r_n$ between two arcs, located symmetrically with respect to the centre and belonging to the same ellipse, and denoting

co-ordinates of the centre of the arc with respect to the ellipse axes as $nh$ (⊥ to the axes $a$) and $y$ (∥ to the axis $b$), we obtain:

$$y = \sqrt{r_n^2 - n^2 h^2}.$$

The canonic equation of ellipse gives

$$a = \frac{xb}{\sqrt{b^2 - y^2}} = \frac{nhb}{\sqrt{b^2 - r_n^2 + n^2 h^2}} \tag{4}$$

where $b$ is the length of the minor axis. Substituting this expression for $a$ in eq. (3), we obtain

$$\cos\theta = \frac{\sqrt{b^2 - r_n^2 + n^2 h^2}}{nh}; \quad \sin\theta = \frac{\sqrt{r_n^2 - b^2}}{nh}. \tag{5}$$

And eq. (2) may be written as

$$C = \frac{nD\lambda}{\sqrt{r_n^2 - b^2}}. \tag{6}$$

Therefore only the number of layer lines up to the given arc should be determined. This requires, however, greatest attention and care in the presence of missing spectra. Let us introduce the relation

$$bd = D\lambda \tag{7}$$

where $d$ is the interplane distance for reflections lying at the ends of the minor axis; this distance may be determined by means of indexing the spot photograph of the zone *hko*. Comparing (6) and (7), we obtain:

$$C = \frac{nd}{\sqrt{\frac{r_n^2}{b^2} - 1}}. \tag{8}$$

When reflections at the ends of the minor axis are absent due to extinction, eq. (7) is used first and only afterwards use is made of eq. (6).

The application of these rules to the determination of the value of $C$ in the case of corresponding electrograms of $CdI_2$ permitted all the operations mentioned above, namely the measurement of $b$ of ellipses and distances between arcs to be made with the accuracy of $\sim 0.3\%$ by means of an electronograph with the constant $D\lambda \simeq 56$ ($D = 1100$ mm, $\lambda = 0.05$ Å and the resolving power $> 700$), thus exceeding the accuracy of analogous measurements by means of X-ray rotation photographs.

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*PHYSICAL CHEMISTRY*

# RELATION BETWEEN THE ENTROPY OF AQUEOUS IONS AND THEIR ELECTROSTATIC CHARACTERISTIC

By A. F. KAPUSTINSKY, Corresponding Member of the Academy

The change of the entropy of ions due to hydration has been studied by Ulich [1], Eley and Evans [2], Latimer [3] and his collaborators. Sakkur deduced a theoretical equation [4] by means of which the entropy of isolated (gaseous) ions can be calculated; Latimer and Eastman [5] suggested semiempirical formulae for calculating the entropy of metals and salts. But up till now no general rules have been given, by means of which it would be possible to estimate an unknown ionic entropy.

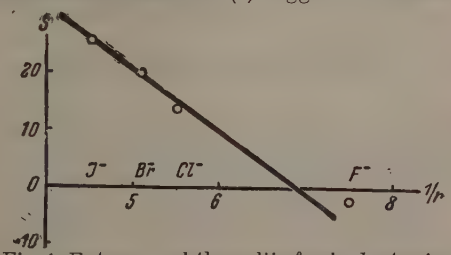

Fig. 1. Entropy and the radii of univalent anions.

The most important of the various forms of interionic bonds in a solution of a strong electrolyte is electrostatic interaction. If we remove the ions reversibly and isothermically from a position of complete contact to a distance greatly exceeding the radius of the ions, viz. to the average distance between ions in a molal solution, we get the work necessary to overcome the electrostatic forces. This work is equal to the corresponding decrease of free energy. The derivative of the free energy by the temperature taken with the inverse sign equals, as we know, the entropy. If we now suppose the entropy of a hydrogen ion to be zero (as is done in electrochemistry, where the free energy of hydrogen is put as zero) and refer the entropy of all the other ions to this value, we shall be able to determine ionic entropy as the thermal coefficient of the energy of electrostatic interaction between ions.

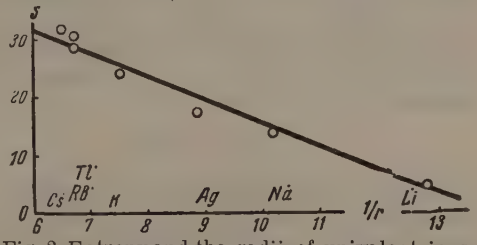

Fig. 2. Entropy and the radii of univalent ions.

Let us turn our attention to equations which express this idea more accurately. Let $e$ be the charge of an electron; $Z$, the valency of the cation; $r$, its radius; $f$, force of its interaction with a hydrogen ion; $A$, the work done; $D$, the dielectric constant of the solvent; $F$, the free energy; $S$, entropy. Let

us examine the process of removing a hydrogen ion from a position of contact with the cation to a distance $a$, equal to the average distance between ions in a molal solution. The hydrogen ion is put at the basis, and all the entropy estimates of other ions are referred to it. The dimensions of the hydrogen ion are negligible in comparison with those of the cation, and therefore in the first position the distance between the centres of charges is practically equal to the radius of the cation

$$dA = fdr.$$

Then

$$A = -\frac{Ze^2}{D}\int_r^a \frac{dr}{r^2} = -\frac{Ze^2}{Dr} + \frac{Ze^2}{Da} \quad (1)$$

$$S = -\frac{d\Delta F}{dT} = \frac{dA}{dT}$$

$$S = \frac{Ze^2}{Dr}\frac{d\ln D}{dT} - \frac{Ze^2}{Da}\frac{d\ln D}{dT}. \quad (2)$$

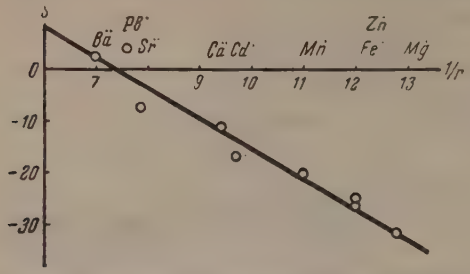


Fig. 3. Entropy and the radii of bivalent ions.

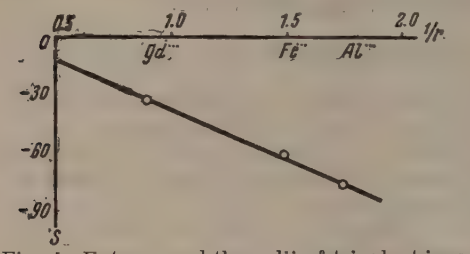


Fig. 4. Entropy and the radii of trivalent ions.

Equation (2) is very sensitive to changes in the dielectric constant of the medium. In this deduction the latter was treated as a continuity which does not change its properties in the field of the ion, which is of course a rough approximation. The «microdielectric» constant is unknown, and so are the dimensions of the ions in solution; therefore in further calculations we make use of Goldschmidt's (Pauling's) ionic radii, obtained by studying crystal lattices.

Thus, in order to check equation (2), it must be reduced to a more simple form. As we know, the temperature coefficient of the dielectric constant of water is negative. Again, the average distance between ions in a molal solution of ions of a given valency $a$ is constant. Therefore instead of (2) we can write:

$$S = -\frac{A}{r} + B. \quad (3)$$

Here $A$ and $B$ are constant for all ions of any given valency. Their numerical values can be established from experimental data on the entropy of aqueous ions.

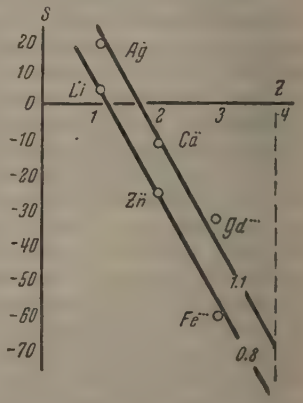


Fig. 5. Relations between entropy and valency.

Equation (3) shows that there is a linear relationship between entropy and the inverse value of the ion's radius. Indeed, as may be seen from the Figs. 2, 3, 4, 5, all the known material on the entropy of aqueous ions agrees excellently with this theoretical deduction. The discrepancies are, with a very few exceptions, all within the limits of experimental error.

It is much more difficult to select ions of equal dimensions, but unequal valencies. However, this is possible, if discrepancies of hundredths of an Å are neglected. Fig. 5 shows the relation between entropy and the valency (i. e.

the charge of the ion) for ions of equal dimensions. The linear nature of this relation is evident. The values of $A$ and $B$ for quadrivalent ions can be found by extrapolating the straight lines.

Determination of the values of $A$ and $B$ makes it possible to calculate the entropy of ions which have not yet been studied in this connexion.

| Valency | of anion | of cations | | | |
|---|---|---|---|---|---|
| $A$ . . . . . | 10.92 | 4.16 | 59.2 | 51.28 | 67.47 |
| $B$ . . . . . | 76 | 56.2 | 44.8 | 14.0 | —3.67 |

Summarizing all the above results we can draw the following conclusions: 1) The entropy of aqueous ions is a thermal coefficient of the energy of electrostatic interaction between ions in solution. 2) The entropy of ions of equal dimensions is a linear function of the ions' charges. 3) The entropy of ions of equal valency is a linear function of the inverse magnitude of the ionic radii.

In concluding, we may note that all the known entropies of aqueous ions given in a summary by Latimer, Pitzer and Smith ([6]) were examined. The entropies of zinc, cadmium and gadolinium ions were taken from the latest papers by Bates ([7]) and Coulter and Latimer ([8]). The entropy of the manganese ion—from a paper by the author, which is being prepared for publication.

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*PHYSICAL CHEMISTRY*

# ENTROPY OF IONS OF THE ELEMENTS OF THE PERIODIC SYSTEM

By A. F. KAPUSTINSKY, Corresponding Member of the Academy

In our preceding paper we examined the problem of the relation between the entropy of aqueous ions and their valency and dimensions. In this paper we intend to find the deviations from this relation more accurately and use this relation to estimate the entropy of all those ions of the periodic table of chemical elements, whose ionic radii are known; ions of higher valency are exceptions, since they do not exist in aqueous solution under any circumstances.

The entropy of univalent anions can be calculated from equation

$$S = -\frac{109.2}{r} + 76; \quad (1)$$

of univalent cations, from equation $S = -\frac{41.63}{r} + 56.2$; (2)

of bivalent cations, from equation $S = -\frac{59.26}{r} + 44.8$; (3)

of trivalent cations, from equation $S = -\frac{51.28}{r} + 14$; (4)

of quadrivalent cations, from equation $S = -\frac{67.47}{r} - 3.67$. (5)

The results of calculations, which were used to plot the curves in the preceding paper, are given in Table 1.

Table 1

Entropy and Ionic Radii

| Ion | Radius | Entropy | | Ion | Radius | Entropy | |
|---|---|---|---|---|---|---|---|
| | | calcul. | exper. | | | calcul. | exper. |
| A. Univalent cations | | | | B. Bivalent cations | | | |
| Lithium . . . | 0.78 | 2.8 | 4.7 | Magnesium . | 0.78 | —31.2 | —31.6 |
| Sodium . . . | 0.98 | 13.7 | 14.0 | Iron . . . . . | 0.83 | —26.6 | —25.9 |
| Silver . . . . | 1.13 | 20.4 | 17.5 | Zinc . . . . . | 0.83 | —26.6 | —25.9 |
| Potassium . . | 1.33 | 24.9 | 24.2 | Manganese . . | 0.91 | —20.3 | —19.1 |
| Thallium . . . | 1.49 | 28.3 | 30.5 | Cadmium . . | 1.03 | —12.7 | —14.8 |
| Rubidium . . | 1.49 | 28.3 | 28.7 | Calcium . . . | 1.06 | —11.1 | —11.4 |
| Caesium . . . | 1.65 | 31.0 | 31.8 | Strontium . . | 1.27 | — 2.0 | — 7.3 |
| | | | | Lead . . . . | 1.32 | 0.1 | 3.9 |
| | | | | Barium . . . | 1.43 | 3.4 | 2.3 |
| C. Trivalent cations | | | | D. Univalent anions | | | |
| Aluminium . . | 0.57 | —76 | —76 | Fluorine . . . | 1.33 | — 7.1 | — 2.3 |
| Iron . . . . . | 0.67 | —62.5 | —61.0 | Chlorine . . . | 1.81 | 14.7 | 13.5 |
| Gadolinium . | 1.11 | —32.0 | —32.5 | Bromine . . . | 1.96 | 19.3 | 19.7 |
| | | | | Iodine . . . . | 2.20 | 25.4 | 25.3 |

Column two gives ionic radii according to Goldschmidt (1); column 3, entropy in calories per g atom per °C, calculated from the interpolation formulae (1—5); column 4 gives entropy according to the summary of experimental values found by Latimer, Pitzer and Smith (2); more recent values are given for zinc and cadmium according to Bates (3); for gadolinium, according to Latimer and Coulter (4); and for manganese, according to data of the author, which are being prepared for publication.

Table 2

| I | II | III | IV | V | VI | VII | |
|---|---|---|---|---|---|---|---|
| $H^{\cdot}$ 0 | | | | | | $F^{-}$ — 2.3 | $Fe^{\cdot\cdot}$ $Co^{\cdot\cdot}$ $Ni^{\cdot\cdot}$ |
| $Li^{\cdot}$ + 4.7 | $Be^{\cdot\cdot}$ — 2.7 | | | | | | —25 —27 —31 |
| $Na^{\cdot}$ +14.0 | $Mg^{\cdot\cdot}$ —31.6 | $Al^{\cdot\cdot\cdot}$ —76 | $Si^{4\cdot}$ —177 | $V^{3\cdot}$ — 65 | | $Cl^{-}$ + 13.50 | $Fe^{\cdot\cdot\cdot}$ |
| | | | | $V^{4\cdot}$ —114 | | | —61 |
| $K^{\cdot}$ +24.2 | $Ca^{\cdot\cdot}$ —11.4 | $Sc^{\cdot\cdot\cdot}$ —48 | $Ti^{3\cdot}$ — 60 | | $Cr^{3\cdot}$ — 65 | $Mn^{2\cdot}$ — 19.1 | |
| | | | $Ti^{4\cdot}$ —109 | | | $Mn^{3\cdot}$ — 59 | $Ru^{4\cdot}$ —108 $Rh^{3\cdot}$ —60 |
| $Rb^{\cdot}$ +28.7 | $Zn^{\cdot\cdot}$ —25.7 | $Ga^{\cdot\cdot\cdot}$ —69 | $Ge^{4\cdot}$ —157 | $As^{3\cdot}$ — 60 | | | |
| | | | | | $Mo^{4\cdot}$ —103 | $Mn^{4\cdot}$ —133 | |
| $Ag^{\cdot}$ +17.4 | $Sr^{\cdot\cdot}$ — 7.3 | $Y^{+++}$ —34 | $Zr^{4\cdot}$ — 81 | $Nb^{4\cdot}$ —101 | | $Br^{-}$ + 19.7 | $Os^{4\cdot}$ —104 $Ir^{4\cdot}$ —106 |
| | | | $Sn^{2\cdot}$ — 4.9 | | | | |
| $Cs^{\cdot}$ +31.8 | $Cd^{\cdot\cdot}$ —16.4 | $In^{\cdot\cdot\cdot}$ —42 | $Sn^{4\cdot}$ — 95 | $Sb^{3\cdot}$ — 43 | $Te^{4\cdot}$ — 79 | $J^{-}$ + 25.3 | |
| | $Ba^{\cdot\cdot}$ + 2.3 | $Tl^{\cdot}$ +30.5 | $Pb^{2\cdot}$ + 3.9 | | $W^{4\cdot}$ —103 | | |
| | | $Tl^{\cdot\cdot\cdot}$ —35 | $Pb^{4\cdot}$ — 84 | | | | |
| | | | $Th^{4\cdot}$ — 65 | | $U^{4\cdot}$ — 67.9 | | |
| | | $Pr^{3\cdot}$ —30 | | | $Sm^{3\cdot}$ — 31 | $Eu^{3\cdot}$ — 31 | |
| $La^{3\cdot}$ —28 | $Ce^{3\cdot}$ —29 | $Pr^{4\cdot}$ —71 | $Nd^{3\cdot}$ — 31 | | | | |
| | $Ce^{4\cdot}$ —70 | | $Ho^{3\cdot}$ — 35 | $Er^{3\cdot}$ — 35 | $Tu^{3\cdot}$ — 35 | $Yb^{3\cdot}$ — 37 | |
| $Gd^{3\cdot}$ —32.5 | $Tb^{3\cdot}$ —33 | $Dy^{3\cdot}$ —34 | | | | | $Lu^{3\cdot}$ — 38 |
| | $Tb^{4\cdot}$ —80 | | | | | | |

Let us examine the discrepancies between the experimental entropy estimates and those calculated by means of the above equations. The accuracy of entropy values for aqueous ions can hardly be taken at present to be greater than one entropy unit. Latimer accepts precisely a value of this order for most of the ions examined by him. This accuracy can be increased to fractions of an entropy unit, but it is apparently not so much the true accuracy of the given value, as the accuracy of the deviations of separate measurements from the average values that increases.

Some of the entropy determinations are quite inaccurate. Thus, the entropy of trivalent ions is given with an accuracy of about 10%, which makes in the case of aluminium, for instance, 10 entropy units. It would seem, that the discrepancies between the calculated and experimental values in the case of lithium and thallium exceed the permissible limits. However, if Ulich's (5) former data are taken into account, we get quite a satisfactory agreement. The same refers to fluorine. The discrepancy for strontium is up to 5 units. But its entropy is calculated by Latimer only on the basis of measuring the heat of solution of the carbonate, as described in a paper by Zimmermann, which was not published (private communication). Possibly, this figure is not as yet final.

No explanations can be offered here for the discrepancies in silver and lead. Apparently, the accuracy with which the entropy of these elements has been determined cannot be put to doubt. They remain outstanding exceptions from the rule discussed in this paper.

These exceptions are so few in number, that the entropy of aqueous ions can be freely calculated for all the elements of the periodic table, whose ionic radii are known according to Goldschmidt (Pauling) (Table 2).

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*PHYSICAL CHEMISTRY*

# IRREVERSIBLE ELECTRODE POTENTIALS OF METALS

By G. B. CLARK and G. V. AKIMOV, Corresponding Member of the Academy

1. Irreversible electrode potentials hold a place of prominence in the field of metal corrosion, since determination of the irreversible electrode potential of the corrosion system is involved in any investigation of the electrochemical mechanism of a corrosion process. The data on irreversible potentials found in various studies on corrosion were obtained under various conditions and by various methods, and are, therefore, often incomparable; systematical works on this subject are few in number ([1–5]).

The purpose of this work was a systematical comparative study of the electrode potentials of various metals in typical electrolyte solution. The electrode potentials of the following 22 metals were determined: Be, Mg, Al, Si, Nb, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn, Cd, Hg, Tl, Sn, Pb, Sb, Bi. Measurements were made in the following solutions: 0.1 *N* HCl; 0.1 *N* $HNO_3$; 0.1 *N* NaOH and 3% NaCl.

In this study we decided not to plot potential—time curves, since such experiments, abstracted from the particular corrosion problem, generally give complicated results which are of little use. However, it was important to take account of the specific behaviour of various metals as regards the formation of their protective films in the air and at the first moments of reaction between the metal and the solution. Therefore it was necessary to determine the electrode potential of the metal after it had been in the solution for some time (standard time in all cases) and the electrode potential of the metal, without its protective film.

2. A series of methods have been reported in literature for measuring the potential after cleaning the metal surface under the solution ([6–10]). We constructed an apparatus shown in Fig. 1, which makes it possible to use samples of various shapes. The sample is fastened at the bottom of a wide glass vessel with an opening by means of a rubber washer «R» and Mendeleeff's wax. The outer end of the sample is clamped in a vice; thus, the sample is held fast, and can be mechanically cleaned while retaining good contact with the measurement circuit. The surfaces of the samples are cleaned under the solution by means of a small carborundum disc *A*, fastened to the pin *T*, made of «textolite» which is a good insulator and is stable in all our media. The carborundum disc is set in motion by an ordinary dentists' drill. The samples were preliminarily polished on paper, freed from grease by means of acetone and alcohol and kept in a desiccator for 24—48 hours. The potentials were measured after 1 and 5 min.,—first, when the solution was agitated

by the carborundum disc*, and then while cleaning the surface under solution. Corrections for liquid potential were not made, since the data at hand gave us grounds to believe that the error so introduced could not possibly exceed 10—15 mV.

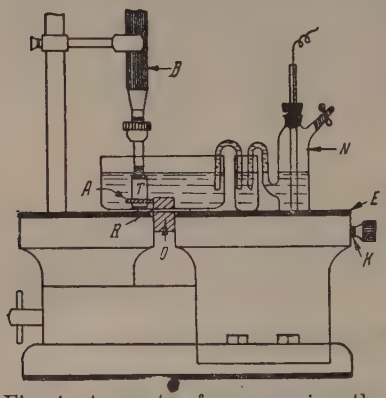

Fig. 1. Apparatus for measuring the potential while cleaning the surface of the samples under solution.

3. By irreversible electrode potentials of metals we mean such electrode potentials at the interface metal—electrolyte, for which the system itself gives no immediate indication as to the nature of the reversible reaction determining the potential. The electrode potentials of metals in solutions of alien ions or in the presence of considerable quantities of such ions, as well as the electrode potentials of solid alloys and the electrode potentials of complex electrodes, all belong, according to this definition, in the group of irreversible potentials. We suggest such a classification of irreversible potentials.

Potentials of the 6th type, i. e. potentials of metals, coated with a protective film, play an important rôle in corrosion. As we know, the behaviour of these electrodes depends greatly upon: 1) the ratio between the area coated

| Various kinds of irreversible electrode potentials | Example |
|---|---|
| Those which can be reduced to reversible potentials of the «1st type» | Zinc in a solution of KCl |
| Those which can be reduced to reversible potentials of the «2nd type» | Copper in a solution of NaOH |
| Reducible to redox potentials | — |
| Reducible to gaseous electrodes | — |
| True potential of the protective film | — |
| Complex electrodes of the film—pore type | Aluminium in a solution of NaCl |
| Potential of solid solutions. Potential of alloys with heterogeneous structure | Potential of Cu—Ni in a solution of NaCl. Potential of the Zn—Cd electrode in a solution of HCl |

with film and that occupied by pores, and 2) the electrical resistance of the film—pore microelement. If the pore area is great enough in comparison with the film area, the electrode can be reduced practically to type 1 or 2. If, however, the pore area is very small or zero, the potential of the electrode should apparently be close to the potential of an inert electrode (under given conditions).

With regard to the resistance of the pore—film microelements, two extreme cases can be distinguished: a) if the resistance of the microelement is high, the value of measured potential will be connected with the potential drop in the anode and cathode parts of the microelement ([11],[12]), b) if, on the other hand, the resistance of the microelement is low, the value of the mea-

* Since the solution is also agitated while the sample is being cleaned, preliminary measurement with agitation makes the action of these two factors qualitatively separable.

sured potential depends on polarization on the anode and cathode areas ([13],[15]).

The properties of the protective film are of great importance. At temperatures of the order of 0—100° a great majority of films, even the very thinnest, are probably impenetrable to the ions (if there are no pores), and therefore the film-coated area cannot possibly act as anode. However, many compounds, including oxides, are known to have marked electronic conductivity even at comparatively low temperatures ([15]).

Since the protective films are thin, it may be assumed that conductive films on the metal may act as cathodes. The cathode reactions can take place on the areas of protective films, because these reactions require only the supply of excess electrons (flowing from the anode). In the case of «non-conductive» films, such as $Al_2O_3$, MgO, the electrons can be transmitted by means of the so called «tunnel effect», provided that the thickness of the film does not exceed a certain value, probably of the order of 50—100 Å ([17]). It may be assumed that cathodic polarization should be stronger in the films of low conductivity than in comparatively conductive films. However, the question is complicated by the fact that low conductivity of the film increases the electrical resistance of the microelements, which decreases the rôle of polarization phenomena.

Electrodes of the «2nd type» are probably capable of high polarization (cathodically), if a considerable part of the slightly soluble corrosion products remain in the form of a protective film on the surface of the metal. The behaviour of electrodes of both the «1st» and «2nd type» in corrosion processes is connected to a great extent with the properties of the reaction product films.

4. In studying the influence of cleaning a section of the metal surface under solution upon its electrode potential Evan's and Mears' polarization diagrams ([13—15]) may be applied. Then, theoretically a number of various cases are possible. Here we shall note only, that cleaning should cause a great change to the negative in the potentials of such metals, which have microcouples of the film (cathode)—pore (anode) type on their surface, and on which the microanodes become greatly polarized due to small anode area. Cleaning should not cause any change in the potentials of pure metals, whose surfaces do not become film-coated (true reversible electrodes of the «1st» and «2nd type», since polarization does not take place in this case. Thus, the change potential to the negative after cleaning is to some extent evidence for the presence of a protective film.

5. The results for 22 metals in 4 media are given in Fig. 2. The points correspond to the potential values taken 5 min. after the metals had been immersed in the solution, which were stirred constantly. The arrows show the magnitude and direction of the change in potential upon cleaning under solution. Besides this, the region of normal reversible potentials is shaded for each metal at 0.001—1 $N$ concentrations of its own ions of the lowest valency.

a) From Fig. 2 it follows that the ability of forming strong protective films decreases in general from the left side of the diagram to the right side. Thus, the most protective films form on metals of the $A$ groups; in these cases cleaning changes the potential of the metal 300—1000 mV to the negative. In the case of the intermediate group cleaning decreases the potential only 200—500 mV, i. e. the film-forming ability of this group is lower. Metals of the 1st group $B$ give films, but the change of potential in this case is much smaller, about 100—200 mV. The rest of the $B$ groups (2—5) form weak protective films almost in all cases, and seldom show negative potential jumps exceeding 100 mV. Of course, the protective films will remain intact on the

metals (or will form in the electrolyte) only if the electrolyte is of the right kind. Thus, a good protective film on Al remains intact in solutions of NaCl,

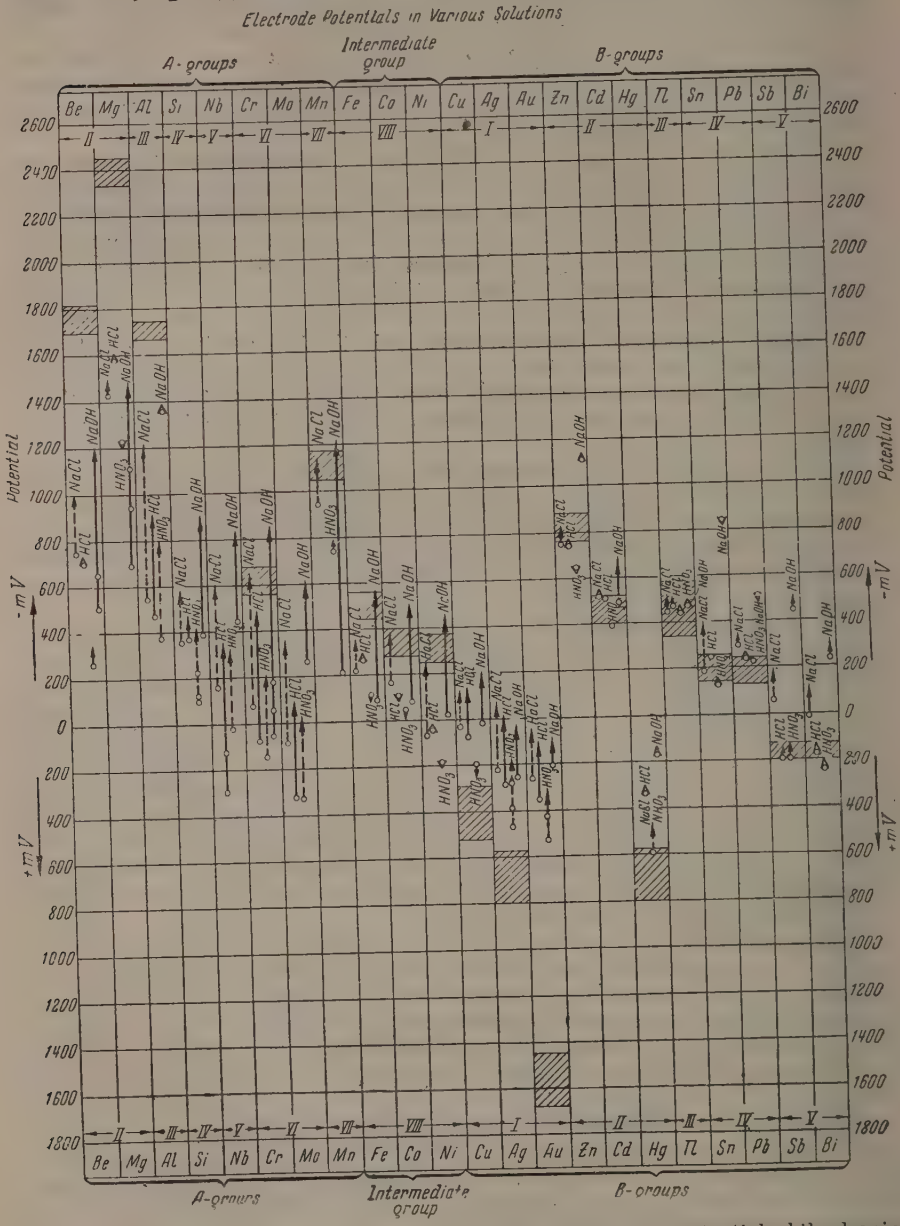


Fig. 2. Base of arrow—potential before cleaning. End of arrow—potential while cleaning. The region of reversible potentials is shaded.

HCl and $HNO_3$, but dissolves in NaOH. Good protective films will form on Mg and Mn only in NaOH, but not in other solutions, etc. The difference in chemical behaviour between *A* group (or intermediate) and *B* group metals

was especially emphasized by Evans ([18]) on the basis of qualitative data; thus, his idea has been confirmed quantitatively in this study.

b) The potential values agree with the pH of the solution only in the case of Sb and Bi.

c) The metals of each group respond similarly to cleaning in spite of the difference in the absolute values of their electrode potentials.

d) The initial electrode potentials (before cleaning) of the *A* group and intermediate metals are more positive, while those of the *B* group metals are more negative than the equilibrium values.

e) The potentials of a number of *A* group and intermediate metals remain unchanged, or are even somewhat «ennobled» upon cleaning. This anomalous behaviour may be due to the following reasons: 1) the film forms so rapidly that we cannot obtain a surface free of film even for a short time; 2) the corrosion process is controlled completely or almost completely by the cathode reaction; 3) stirring, while cleaning goes on, greatly reduces cathodic polarization when the process is controlled both by the anode and cathode reactions.

f) The following assumption can be made as to the nature of the electrode potentials of the metals investigated.

Metals of the *A* group and intermediate metals in most of the typical solutions form complex electrodes of the film—pore type, where the pore may act as electrode of the «1st» or the «2nd type» in accordance with the solubility product of the compounds formed as a result of the reaction between the metal and the solution.

The metals of group 1*B* in most cases form a complex electrode of the film—pore type (electrode of the «2nd type»). The rest of the metals of the *B* group form preferentially simple electrodes of the «1st» or «2nd type». On these metal films have been revealed by cleaning only in a few cases.

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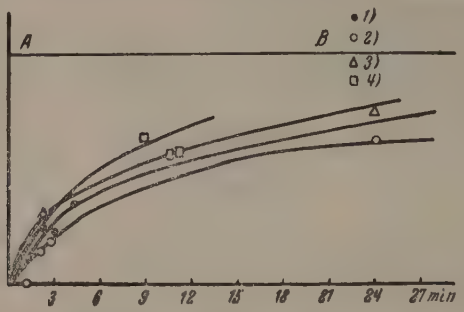
*PHYSICAL CHEMISTRY*

# ON THE SOLVATE EXCHANGE IN MIXED SOLVENTS

By A. E. POLESSITSKY and F. L. TEMERLIN

*(Communicated by V. G. Chlopin, Member of the Academy, 29. XII. 1940)*

Using radioelements as indicators, one has recently succeeded to discover a very intensive exchange of the free ions in the solution with the same ions bound in the complexes (1), as well as with the ions of the precipitates (2). The same effect takes place in mixed solvents (see later). Such a slow exchange of the solvating particles, as described in articles by Roginsky and collaborators (3), can therefore scarcely be imagined.




We have made experiments of the same type: a solution of NaBr in $H_2O$ was mixed under intensive stirring with a solution of NaBr in $C_2H_5OH$. One of the solutions, marked by an asterisk, contained some radioactive bromine Br*. Several equal portions of AgBr were quickly precipitated from the mixed solution and investigated for radioactive bromine. The results obtained with different temperatures, concentrations of NaBr and relative volumes of the solvents are given in Table 1.

Table 1

| Solvents | $T$°C | Duration of exp. in min. | Activity of the fractions of AgBr | | | |
|---|---|---|---|---|---|---|
| | | | I | II | III | IV |
| $H_2^*O - C_2H_5OH$ | + 15 | 17 | 685 | 630 | 600 | 620 |
| $H_2^*O - C_2H_5OH$ | + 15 | 16 | 290 | 310 | 300 | 340 |
| $H_2^*O - C_2H_5OH$ | — 20 | 16 | 440 | 380 | 390 | 380 |
| $H_2^*O - C_2H_5OH$ | — 22 | 14 | 570 | 530 | 530 | 500 |
| $H_2O - C_2H_5^*OH$ | + 15 | 15 | 270 | 298 | 292 | 280 |
| $H_2O - C_2H_5^*OH$ | + 15 | 12 | 320 | 230 | 250 | 250 |
| $H_2O - C_2H_5^*OH$ | 0 | 16 | 620 | 640 | 600 | 690 |
| $H_2O - C_2H_5^*OH$ | + 15 | 12 | 1 233 | 1 130 | 1 080 | — |

These data show neither a drop of the activity from the first fraction to the last one, in the case when the radioactive bromine was added to the $H_2O$ solution, nor a rise of the activity in the inverse case. All fractions show the same activity, which points to the solvate equilibrium.

The results obtained with other solvents are summarized in Table 2. In some experiments there was prepared a large quantity of the mixed solution, separate portions of which were taken at different intervals to precipitate some fractions of AgBr.

Table 2

| Solvents | Duration of experiment | Activity of the fraction of AgBr | | | |
|---|---|---|---|---|---|
| | | I | II | III | IV |
| $H_2^*O$—$CH_3OH$ | 14 min. | 290 | 290 | 286 | 260 |
| $H_2^*O$—$CH_3OH$ | 14 » | 1370 | 1260 | 1420 | 1220 |
| $H_2^*O$—$CH_3OH$ | 15 » | 350 | 380 | 345 | 310 |
| $H_2O$—$CH_3^*OH$ | 14 » | 355 | 365 | 290 | 308 |
| $H_2O$—$CH_3^*OH$ | 15 » | 345 | 335 | 320 | 305 |
| $H_2O$—$CH_3^*OH$ | 7 » | 520 | 470 | 470 | — |
| » » | 2 hrs after the mixing | 410 | 390 | 380 | — |
| $H_2^*O$—$(CH_3)_2CO$ | 7 min. | 832 | 855 | 783 | — |
| $H_2^*O$—$(CH_3)_2CO$ | 9 » | 600 | 605 | 660 | — |
| $H_2O$—$(CH_3^*)_2CO$ | 7 » | 520 | 540 | 500 | — |
| $H_2^*O$—$(CH_3)_2CO$ | 2 min. after the mixing | 123 | 131 | 131 | — |
| » » | 8 » » » » | 123 | 135 | 116 | — |
| » » | 22 » » » » | 140 | 123 | 115 | — |
| » » | 60 » » » » | 116 | 81 | 87 | — |
| $H_2O$—$(CH_3^*)_2CO$ | 2 » » » » | 200 | 215 | 270 | — |
| » » | 60 » » » » | 270 | 250 | 300 | — |
| $H_2^*O$—$C_3H_8O_3$ | 20 min. | 123 | 115 | 100 | 100 |
| $H_2^*O$—$C_3H_8O_3$ | 20 » | 270 | (363) | 300 | 280 |
| $H_2^*O$—$C_3H_8O_3$ | 24 » | 170 | 160 | 150 | 170 |

No difference in the activity of the subsequent fractions of AgBr was observed in these experiments either. Under the described conditions the solvate equilibrium seems to be reached rather quickly.

The exchange of the bromine ions between the solutions of NaBr in mixed solvents and solid AgBr is illustrated in the figure.

The activity of the precipitate quickly rises to the line *AB* corresponding to the full exchange. The exchange with the precipitate formed in the same solution must proceed at a still higher rate, especially in the first stage, when the precipitate is in the submicrone state. Under such condition it is very difficult to obtain precipitates sharply differing in their activities.

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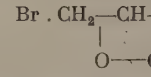
*CHEMISTRY*

# β-LACTONE OF TRICHLOROETHYLIDENE-MALONIC ACID

By M. M. SHEMIAKIN and N. S. WULFSON

*(Communicated by N. D. Zelinsky, Member of the Academy, 7. XII. 1940)*

In a former paper (1) dealing with the condensation of bromoacetaldehyde with malonic acid we succeeded in showing that instead of the expected bromoethylidene-malonic acid the formation of its β-lactone took place:



Assuming that an increase of the amount of halogen atoms would promote the formation of β-lactoacids of this kind, we selected chloral as our next object for the study of this reaction.

The first to condense chloral with malonic acid was Garzarolli Thurnlackh, who in 1891 heated the two compounds in acetic acid (2). The compound obtained was characterized as γ-trichloro- β-hydroxybutyric acid (IV). In 1905 Doebner and Segelitz (3) carried out this condensation in pyridine and obtained better yields. In 1907 Kötz (4) subjected ethyl trichloro-ethylidene-malonate to hydrolysis by refluxing the ester with 27% hydrochloric acid and isolated a substance which was described by him as γ-trichlorocrotonic acid (I), which had the same m. p. as the acid obtained previously by Garzarolli Thurnlackh. However, in 1913 Auwers and Schmidt (5) discovered in the calculations of the analysis by Kötz a mistake and identified the acid prepared by that author as γ-trichloro-β-hydroxybutyric acid (IV), already known. Auwers and Schmidt prepared esters of this acid, as well as its acetyl derivative formed when the acid was refluxed with acetyl chloride.

We carried out the condensation of chloral hydrate with malonic acid in piperidine and acetyl acid and obtained at a temperature of about 100° a good yield (80%) of a white crystalline substance, that after crystallization from benzene had m. p. 118—119°, i. e. the same melting point as the acids obtained by the above-mentioned authors. Direct titration with a 0.1 *N* sodium hydroxide solution showed this substance to be a monobasic acid, whereas after refluxing it with an excess of a 0.1 *N* alkali solution titration showed it to be a dibasic acid. Silver salts were successfully prepared, both for the monobasic and the dibasic acids. The analytical data are compared in the following table with data calculated for all the possible structural formulae that could be ascribed to the condensation product.

On the basis of analytical data we came to the conclusion that the substance synthetized by us was the β -lactone of trichloroethylidene-malonic acid which when heated with an alkali solution underwent a rupture of the ring with the formation of trichloroethylidene-malonic acid.

In order to prove that the acid obtained by us was identical with the one obtained by Auwers and Schmidt and by Doebner and Segelitz, we carried out the reaction keeping strictly to conditions described by these authors.

| No | Formula | Name | Titration of a weighed sample 0.1256 g in cm³ of 0.1 N NaON | % Cl | % Ag |
|---|---|---|---|---|---|
| I | $Cl_3C-CH=CH-COOH$ | γ-trichlorocrotonic acid | 6.62 | 70.75 | 36.40 |
| II | $Cl_3C-CH=C(COOH)_2$ | Trichloroethylidene-malonic acid | **10.74** | **45.61** | **48.20** |
| III | $Cl_3C-CH(O-CO)-CH-COOH$ | β-lactone of trichloroethylidene-malonic acid | **5.37** | **45.61** | **31.69** |
| IV | $Cl_3C-CH(OH)-CH_2\cdot COOH$ | γ-trichloro-β-hydroxybutyric acid | 6.04 | 51.33 | 34.31 |
| V | $Cl_3C-CH(OH)-CH(COOH)_2$ | (β-trichloro-α-hydroxyethyl)-malonic acid | 9.97 | 42.34 | 45.37 |

| | Titration | | % Cl | Precipit. | |
|---|---|---|---|---|---|
| | in the cold | after boiling | | in the cold | after boiling |
| Analytical data | 5.29 | 10.58 | 45.57 | 31.56 | 47.73 |

In both cases a product melting at 118—119° was obtained, that gave no depression of the melting point when mixed with our lactoacid. When titrated in the cold, this product seemed to be monobasic, and after boiling with an alkali solution—dibasic. This made it possible to draw the conclusion that the acid isolated by Garzarolli Thurnlackh, and later described by Doebner-Segelitz and Auwers-Schmidt was not γ-trichloro-β-hydroxybutyric acid, but the β-lactone of trichloroethylidene-malonic acid.

The preparation by Auwers and Schmidt of the esters and the acetyl derivative of trichlorohydroxybutyric acid does not contradict the formula proposed by us for this condensation product, as both etherification in the presence of HCl and acetylation with acetyl chloride would be accompanied with the cleavage of the lactone with simultaneous decarboxylation. In fact, acetylation of the lactoacid, obtained through condensation in piperidine and acetic acid, as well as of that obtained under conditions of Auwers and Schmidt, invariably yielded the acetyl derivative of γ-trichloro-β-hydroxybutyric acid (m. p. 96—97°) and, besides, during the reaction it was possible to detect carbon dioxide, 94% of the theoretical amount.

Thus, it can be considered as proved that the condensation of chloral with malonic acid yields the β-lactone of trichloroethylidene-malonic acid. The structural formulae proposed formerly for this compound by other authors should be considered erroneous.

Synthesis of the β-lactone of Trichloroethylidene-malonic Acid (III). I. 16.5 g of chloral hydrate and 10.4 g of malonic acid were dissolved in 50 cm³ of glacial acetic acid, and 5 cm³ of piperidine were added, this being accompanied by a considerable evolution of heat. The reaction mixture after standing for 2 hours was heated for 4 hours on a steam bath and poured into 100 cm³ of 10% sulphuric acid, extracted with ether, dried over calcium chloride, and the ether dis-

tilled off. The residue crystallized, and after recrystallization from benzene a crystalline substance (m. p. 118—119°) was obtained. Yield 80%*.

Analysis. 1) Titration of the β-lactoacid (III): weighed portion—0.1256 g; used 0.1 *N* NaOH when titrating in the cold—5.29 cm³; calculated for the β-lactoacid (III)—5.37 cm³; used 0.1 *N* NaOH after boiling with an alkali solution—10.58 cm³; calculated for (II)—10.74 cm³.

2) Silver salt precipitated with $AgNO_3$ from the aqueous solution after neutralization with sodium hydroxide in the cold [silver salt of the β-lactoacid (III)]: weighed portion—0.3611 g; obtained AgCl—0.1514 g; found Ag %—31.56; calculated for the β-lactoacid (111) Ag %—31.69. Silver salt precipitated with $AgNO_3$ from the aqueous solution after boiling the latter with two equivalents of the alkali [silver salt of ethylidene-malonic acid (II)]: weighed portion—0.0541 g; obtained AgCl—0.0343 g; found Ag %—47.73; calculated for the trichloroethylidene-malonic acid (II) Ag %—48.20.

3) Determination of chlorine according to Stepanov in the β-lactoacid (III): weighed portion—0.3387 g; used 0.1 *N* solution of $AgNO_3$—43.48 cm³; found Cl %—45.57; calculated for $C_5H_3O_4Cl_3$—Cl % 45.61.

II. When the reaction was carried out under conditions described by Auwers and Schmidt ([5]), the yield was 26.5%; m. p. (after crystallization from benzene) 118—119°. No depression of the melting point was observed when a sample was mixed with the acid obtained in experiment I.

Titration of this acid: weighed portion—0.0627 g; used 0.1 *N* NaOH when titrated in the cold—2.72 cm³; calculated for the β-lactoacid (III)—2.68 cm³; after boiling with an alkali solution, used 0.1 *N* NaOH—5.53 cm³; calculated for trichloroethylidene-malonic acid (II)—5.36 cm³.

III. When the condensation was carried out under conditions of Doebner and Segelitz ([3]), the yield was 60.8%; m. p. (after crystallization from benzene) 118—119°; no depression of the melting point being observed when mixed with the acids described in experiments I and II.

Titration of this acid: weighed portion—0.0962 g; used 0.1 *N* NaOH when titrated in the cold—4.17 cm³; calculated for the β-lactoacid (III)—4.12 cm³; after boiling with an alkali solution, used 0.1 *N* NaOH—8.35 cm³; calculated for trichloroethylidene-malonic acid (II)—8.24 cm³.

Acetylation of the β-lactoacid (III). 1 g of the β-lactoacid and 2 g of acetyl chloride were refluxed on a water bath. The reaction was accompanied by a violent evolution of gas. The evolving gases were collected over a saturated sodium chloride solution. After one and a half hours air was flown through the reaction mixture in order to eliminate the remaining traces of $CO_2$. In all, 246 cm³ of gas were obtained. After a two-fold absorption with a 40% KOH solution, 153 cm³ of the gas remained. Therefore in this reaction the evolution of 93 cm³ of $CO_2$ (94%) had taken place. The excess of acetyl chloride was distilled off from the reaction mixture, and the thick brown paste was left standing for some days, until it crystallized. After recrystallization from ligroin, m. p. 96—97° (this corresponding to the melting point described by Auwers and Schmidt).

Titration: weighed portion—0.0638 g; used 0.1 *N* NaOH—2.45 cm³; calculated for γ-trichloro-β-acetohydroxybutyric acid ($C_6H_7O_4Cl_3$)—2.57 cm³.

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*Translated by A. Plate.*

* When the condensation was carried out in the presence of piperidine without acetic acid, the yield was 60%.

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*CHEMISTRY*

# ON THE LIQUID ACIDS FROM THE FATTY OIL OF LYCOPODIUM *(LYCOPODIUM CLAVATUM)*

By M. V. TSAREV

*(Communicated by N. D. Zelinsky, Member of the Academy, 2. I. 1941)*

The first paper in this field belongs to Langer (1). This author established the fact that the spores contained 49.34% of oil. The liquid fatty acids obtained from the oil of fresh and old spores were of a different composition. The liquid acid from fresh spores Langer characterized as a monobasic carboxylic acid, with an empirical formula $C_{16}H_{30}O_2$, having the structure of α-decyl-β-isopropyl-acrylic acid, and he called this acid Lycopodiumölsäure (lycopodium-oleic acid). The acid isolated from old spores had the composition $C_{16}H_{30}O_3$ and was the oxidation product of the first acid. The liquid acids formed in both cases the major part of the oil (80—86.67%) (2).

In 1889 a paper by Bykovsky appeared on the constituents of the oil from the lycopodium spores (3). According to his investigations, the spores contained 48.5% of a fatty oil, the main part of which being oleic acid $C_{18}H_{34}O_2$ (80%). After the publication of Bykovsky's paper Langer published a third paper (4) dealing with the acid isolated from the lycopodium spores, in which he proposed to leave open the question concerning the normal or branched structure of this acid.

Rathje (5) succeeded in isolating 49.3% of a fatty oil from the spores, of which 81% by weight were a liquid acid. The iodine value determined by this author, 98.7, as well as the equivalent (molecular) weight determined through the neutralization value 256.8, and through combustion of the silver salts, 264,1, made him conclude that Langer was correct in his assumption.

In the literature on fatty oils this acid $C_{16}H_{30}O_2$ has been considered up to the present as an individual substance and known by the name of «lycopodium acid».

Our study has proved that the fatty oil isolated from lycopodium spores as well as the fatty acids of the fatty oil, have physical-chemical constants very near those described by other authors. This gives us full right to make the conclusion that the oil investigated by us is similar in its chemical composition to the oil investigated by Langer and Rathje. However, we have proved that the fatty oil of lycopodium contains two unsaturated acids—oleic and linoleic acids. Lycopodium-oleic acid $C_{16}H_{30}O_2$ described by Langer as α-decyl-β-isopropyl-acrylic acid is not to be found in the fatty acid of lycopodium and was reported by Langer erroneously.

To obtain the fatty oil in order to determine its physical-chemical constants, lycopodium spores were ground for a long time against quarz sand and extracted with ether. The physical-chemical constants of the fatty oil, as determined by us and by Rathje, are given in the table.

| | Specific weight | Refractive index | Saponification value | Iodine value | Reichert-Meiss value | Acetate number | Gener. number | Acid value |
|---|---|---|---|---|---|---|---|---|
| Rathje . . | 0.9360 | 1.467 | 195 | 81 | 7.3 | 44 | 87.6 | 18.6 |
| The author | 0.9321 | 1.4705 | 191.3 | 80 | 5.2 | 31.5 | — | 17.7 |

By comparing the constants of the fatty oil it may be seen that the oil isolated by us was almost identical with the fatty oil previously investigated by other authors (Rathje).

In order to obtain the fatty acids more rapidly, a chemical method for the destruction of lycopodium spores has been devised by us. The extraction of fatty acids was carried out in the following manner: 785 g of lycopodium spores were placed in a 5-liter flask, 3.5 l of 40% potassium hydroxide were added and the mixture was heated for 2.5 hrs on a water bath, this being followed by filtration. Potassium soaps obtained in an alkaline solution were decomposed with 30% $H_2SO_4$, and the fatty acids were extracted with ether. In this way 131 g of fatty acids were obtained, this being 16.7% to the weight of the spores used.

For the extraction of the potassium salts of fatty acids remaining in the spores, the latter were wetted with 30% $H_2SO_4$, dried in the air and extracted with ether. Thus, 159 g of fatty acids were isolated in addition to those obtained previously, the total yield being 290 g, or 37% by weight of the spores used for analysis. The fatty acids were transparent and coloured dark yellow. The separation of the acids was effected by the Twitchell method ([6]). From 150 g used for the separation of the acids 126.5 g of liquid and 12.9 g of solid acids were obtained.

The physical-chemical properties of the fatty acids were as follows: $d_{20}$—0.9101; $h_D^{20}$—1.4615; iodine value 97.5; neutralization value 202.7. According to the investigations of Langer, $d_{20}$—0.9053; neutralization value 218. According to Rathje, iodine value 98.7; neutralization value 218.8.

The equivalent weight of the isolated liquid acids was determined by the method of the combustion of their silver salts and by determining the neutralization value. The combustion of the silver salts gave following:

Weighed portions: 0.0935; 0.1062 g; obtained Ag 0.0270; 0.0300 g. % Ag: 28.27; 28.26; average % Ag 28.265. Molecular weight found 275.

Determination of the equivalent weight by the titration method:

Weighed portions: 1.8332; 2.1360 g; used for titration 0.1 *N* KOH 65.83; 76.78 cm³. Molecular weight found 279; 275; average 277.5.

Content of silver in the salts of the liquid acids of the lycopodium oil, according to other investigators, was as follows: determined by Langer 29.17% Ag; Rathje 29.03% Ag and Bykovsky 28.73% Ag. Calculated for $C_{16}H_{29}O_2Ag$—29.91% Ag; for $C_{18}H_{34}O_2Ag$—27.76% Ag.

On the basis of this data, Bykovsky ([3]) classified the liquid acid, the molecular weight of which corresponded to the empirical formula $C_{18}H_{34}O_2$, as oleic acid. Langer and Rathje classified it as an acid with the empirical formula $C_{16}H_{30}O_2$ and named it lycopodium-oleic acid.

The molecular weight computed by us both by the method of the combustion of silver salts (275) and the titration method (277.5) was somewhat lower than the molecular weight of oleic (282) and linoleic acids (280) and much higher than the molecular weight of lycopodium-oleic acid (254).

The elaidine test gave positive results.

B r o m i n a t i o n. Before bromination the isolated liquid acids were subjected to a second purification according to Twitchell. Bromination was

carried out by adding an ether solution of bromine to a cold solution of the liquid acids in a mixture of ether and glacial acetic acid. After the elimination of the solvent, crystals poorly soluble in petroleum ether appeared upon the surface of the orange bromide having the aspect of an ointment. In this way two bromides were obtained—a poorly soluble crystalline one and a well soluble liquid one. After two crystallizations of the solid bromide from petroleum ether lustrous plates were obtained, m. p. 113—114°.

Bromine determination according to Stepanov:

Weighed portions: 0.1578; 0.1818 g; used for titration 0.1 *N* $AgNO_3$ 10.50; 12.16 cm³. Found 53.2; 53.46%. Calculated for $C_{18}H_{32}O_2Br_4$ — 53.33% Br.

The melting point and the percentage of bromine in the bromide showed that the solid bromide obtained was the tetrabromide of linoleic acid, the melting point of the latter being 114—115°. The remaining liquid bromide was coloured yellow and contained 36.40% Br.

Weighed portions: 0.3070; 0.3558 g; obtained AgBr 0.2626; 0.3051 g. Found 36.38; 36.42% Br. Calculated for $C_{18}H_{34}O_2Br_2$ — 36.3% Br; for $C_{16}H_{30}O_2Br_2$—38.75% Br.

On the basis of the percentage of bromine the liquid bromide should be classified as the bromide of oleic rather than lycopodium-oleic acid.

Langer had also obtained an unctuous bromide, but he did not succeed in isolating the tetrabromide. The bromide obtained by Langer contained only 34.7% Br. Because of the low bromine content he was obliged to classify it as the bromide of a hydroxyacid $C_{16}H_{30}O_3Br_2$, though the latter should contain 37.3% Br.

Oxidation. Through the oxidation of the liquid acids by the method of Gazura ([6]) crystalline hydroxyacids of white colour were obtained. Using the method of fractional crystallization, a series of fractions were isolated with melting points from 136 to 169°. From the hydroxyacids two most characteristic ones were obtained: 1st fraction—a hydroxyacid, crystallizing from alcohol in lustrous plates, m. p. 129—130°, molecular weight 318.5.

Weighed portions 0.0732; 0.0642 g; used for titrations 0.1 *N* KOH 2.30; 2.02 cm³. Found molecular weight 319; 318; average 318.5.
Calculated for $C_{18}H_{34}O_2(OH)_2$ molecular weight 316.

By comparing the melting point and the molecular weight of the isolated fraction with the melting point of dihydrostearic acid (131°), we came to the conclusion that this hydroxyacid was actually dihydroxystearic acid (oxidation product of oleic acid). The second fraction, smaller by weight, after crystallization from alcohol had a m. p. 154—169°.

Weighed portion 0.0916 g; used for titration 0.1 *N* KOH 2.61 cm³.
Found mol. weight 350.5. Calculated for $C_{18}H_{32}O_2(OH)_4$ molecular weight 348.

The constants of the second fraction characterize it as a tetrahydroxystearic acid (oxidation product of β-linoleic acid). M. p. of β-sativinic acid 173°.

Thus, it may be considered as proved that the liquid acids of lycopodium oil consist of a mixture of two acids—oleic acid 91.7% and linoleic acid 8.3%. The percentage was computed on the basis of the iodine value of the mixture acids.

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*CHEMISTRY*

# FUSIBILITY DIAGRAM OF THE SYSTEM LiF—KF—$MgF_2$

By A. G. BERGMAN and S. P. PAVLENKO

*(Communicated by N. S. Kurnakov, Member of the Academy, 4. I. 1941)*

The ternary system LiF—KF—$MgF_2$ was studied after the visual-polythermic method. The temperature at which the first crystals formed and that at which the last ones disappeared were determined by means of a thermocouple Pt/Pt, Rh, whose bared joint was submerged in the melt in a platinum crucible which was placed in an electric blast-furnace and illuminated from above by means of a light with a reflector.

Of the three component binary systems we studied the system KF—$MgF_2$ for the first time. In this system we found: a compound $KF.MgF_2$ with an open maximum on the composition—temperature diagram, having a melting point of 1054° C; and a transition point with 870° and 22 Mol% $MgF_2$, belonging to the incongruently melting compound $2\,KF.MgF_2$. The eutectic points are: 1) at 1004° and 69.7% $MgF_2$; 2) at 786° and 14% $MgF_2$.

The system LiF—KF was studied by A. G. Bergman and E. P. Dergunov. The results obtained previously were checked and confirmed. LiF and KF form an eutectic with 490° and 50.5% LiF. The system LiF—$MgF_2$ was found to have a minimum on the curve of continuous solid solutions with 742° and 33% $MgF_2$. The existence of a minimum at 45% $MgF_2$ and 669°, as reported by Taccini [1], must be rejected. When 5—6% of KF are added, the continuous solid solutions within the ternary system change to limited solutions, and there appears an equilibrium curve.

For plotting the full surface of the liquidus 10 sections were made within the triangle of equilibrium. The general form of the state diagram of the system LiF—KF—$MgF_2$ is given in Fig. 1. The composition triangle is divided into five areas by the boundary lines between $KF.MgF_2$ (56.1% of the whole area), $2KF.MgF_2$ (5.8%), $MgF_2$ (22.4%), LiF (10.3%) and KF (5.4%). Attention is invited by the fact that the field of the compound $KF.MgF_2$ occupies an extraordinarily large area on the composition triangle, although the melting point of this compound (1054°) is lower than that of $MgF_2$ (1270°).

The boundary between the fields of LiF and $MgF_2$, which form a continuous series of solid solutions, is incomplete, but they can be divided conventionally by continuing the line of decomposition of solid solutions to the side LiF—$MgF_2$.

The formation of the compounds $2KF.MgF_2$ and $KF.MgF_2$ divides the composition triangle up into three ternary systems:

I. $KF - 2KF \cdot MgF_2 - LiF$
II. $2KF \cdot MgF_2 - KF \cdot MgF_2 - LiF$
III. $KF \cdot MgF_2 - MgF_2 - LiF$

Therefore there are two eutectic and one transitional triple points in the system. The triple point of the phase triangle KF—LiF—$2KF.MgF_2$ has a melting—solidification temperature of 488°, which is 2° less than the eutectic temperature of the double system LiF—KF. The boundary line comes right up to the double eutectic LiF—KF. There is also a triple transitional

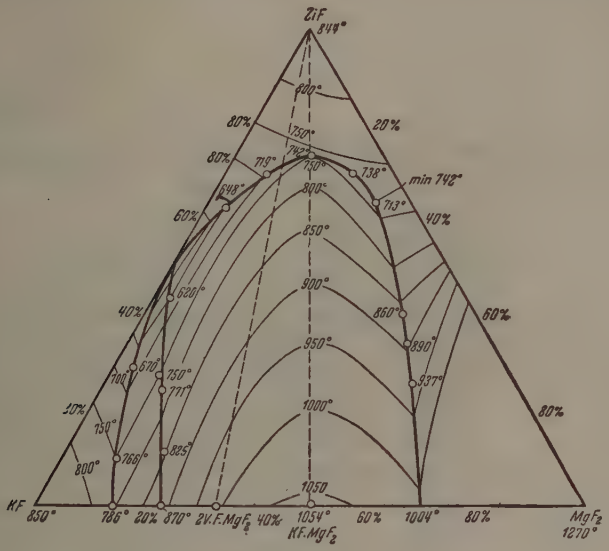


Fig. 1.

point in this vicinity, whose exact position we have not been able to establish, due to the gradual degeneration of the boundary line between the fields of $2KF.MgF_2$ and $KF.MgF_2$ in the direction from the side KF—$MgF_2$ to the triple point. The melting—solidification temperature of the triple point in the phase triangle LiF—$MgF_2$—$KF.MgF_2$ is 713° and its composition is 63.5 Mol % LiF, 30.5 Mol % $MgF_2$ and 6 Mol % KF.

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*GEOCHEMISTRY*

# ON THE RÔLE OF ZIRCONIUM IN MINERALS OF NEPHELINE-SYENITE MASSIFS

By V. I. GERASSIMOVSKY

*(Communicated by A. E. Fersman, Member of the Academy, 10. I. 1941)*

The rocks building up nepheline-syenite massifs are usually subdivided by investigators into two groups. The agpaite group in which the ratio of the number of $K_2O+Na_2O$ molecules to the number of $Al_2O_3$ molecules is greater than unity, and the miaskite group in which this ratio equals or is smaller than unity. Complex zircono-silicates (eudialite, eucolite, etc.) are characteristic of agpaite rocks, whereas miaskite rocks are characterized by the presence of zircon, an exception being the Mariupol massif. This massif is built up of rocks of the agpaite type, but instead of complex zircono-silicates they contain zircon.

E. E. Kostyleva (1) recently discussed the question why the nepheline-syenite massifs contain zircon in some cases and complex zircono-silicates in others. This author believes that the formation of complex zircono-silicates requires not only a surplus of alkalies over $Al_2O_3$, but also a considerable concentration of volatiles in the magma, from which the rocks containing these volatiles were formed. Kostyleva further assumes that «no considerable polymerization of silicate molecules occurs in the case of a surplus of alkalies being present and volatiles, playing an insignificant rôle in the magma, or during differentiation and solidification of magma under reduced pressure. Therefore, zircon instead of zircono-silicates would be formed».

The formation of zircon in some cases and complex zircono-silicates in others depends primarily upon the quantitative relation of alkalies, $Al_2O_3$ and $SiO_2$, and not upon the ratio of volatile constituents only. That these latter played a significant rôle, for example, in the process of formation of the Mariupol alkaline massif is demonstrated by the phenomena of sodalitization, cancrinitization, ceolitization, kaolinization and formation of fluorite, discussed also by Kostyleva. However, no complex zircono-silicates are encountered in this massif, only zircon being present. Therefore the volatile constituents cannot be considered as the cause of complex zircono-silicates in agpaite rocks (the Chibiny and Lovozero massifs) on the one hand, and of zircon (the Mariupol massif) on the other, for in both cases the volatiles played a significant rôle in the processes of mineral formation.

The agpaite rocks of the Chibiny and Lovozero massifs, containing zirconium minerals, are less acid than the agpaite rocks of the Mariupol massif. The acid number $\alpha$ of the former varies from 1.72 to 1.97 and that of the Mariupol rocks from 1.99 to 2.51. Hence, the environment for zirconium during formation of rocks of the Chibiny and Lovozero massifs was different from that of the Mariupol massif. That zirconium in the Chibiny and Lovozero alkaline massifs may appear as anion, thus compensating the scarcity of silica

(as compared to the Mariupol massif) and forming together with $SiO_2$ complex zircono-silicates (eudialite, eucolite, etc.), is highly probable. In the Mariupol massif which is more acid, the relation of the acid part to the bases is different, and zirconium, under these conditions, plays the opposite rôle appearing as cation, and is contained in zircon*.

No discussion of mineral formation problems can be based solely on the agpaite number, because it is not indicative of general relations between the main oxides constituting the minerals which build up the massifs. And it seems also very unlikely that the acid number $\alpha$ might fully represent the nature of mineral formation processes in the case of alkaline massifs, as, according to F. J. Loewinson-Lessing, it expresses the ratio of the number of oxygen atoms associated with silicon to the number of oxygen atoms in all bases including sesquioxides. In the alkaline massifs the sesquioxides $Al_2O_3$ and $Fe_2O_3$ should not, perhaps, be considered as bases, but rather as complex (with $SiO_2$) acid radicals. Therefore, in the case of alkaline massifs preference should probably be given to the coefficient expressing the ratio of bases $(R_2O+RO)$, on the one hand, and acid radicals $(R_2O_3+RO_2)$, on the other. The ratio $\frac{R_2O+RO}{R_2O_3+R_2O}$ for rocks containing the zirconium minerals of the Chibiny and Lovozero massifs varies from 0.23 to 0.27; for the Mariupol massif, from 0.17 to 0.22; and finally for the Vishnevogorsk massif it equals approximately 0.20. Zircon is encountered in the last two massifs, while complex zircono-silicates are observed in the first two massifs.

In conclusion it should be pointed out that the ratio $\frac{R_2O+RO}{R_2O_3+RO_2}$ for the Chibiny foyalite (0.23) is very close to that found for the gneiss-like mariupolite of the Mariupol massif (0.22). This proximity is displayed by the fact that zircon occurs sometimes in the Chibiny foyalite together with complex zircono-silicates. The agpaite number of foyalite is unity and that of the gneiss-like mariupolite 1.27. If the mineralogical composition of the rocks were stipulated by alkalinity alone, the foyalite should, considering the agpaite number, contain zircon, while the gneiss-like mariupolite should contain complex zircono-silicates. As a matter of fact, the case is reverse and we find zircon in mariupolite, whereas in foyalite complex zircono-silicates and partly zircon are contained. This is a stricking example showing that the mineralogical composition of rocks is determined not only by the ratio of alkalies to alumina, or by the rôle of volatile constituents, but primarily by the quantitative ratio of all main elements of the melt, from which the agpaite rocks were formed.

The conclusion to be drawn from what has been exposed here is that zirconium (an amphoteric element) in nepheline-syenites performs different functions according to the conditions available. In a more acid environment (or in the presence of surplus of alkalies) it appears as cation and forms zircon ($ZrSiO_4$); in a less acid environment, together with silicon, it plays the rôle of a complex anion in eudialite, eucolite and other complex zircono-silicates.

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* K. A. Vlasov remarked during discussion on E. E. Kostyleva's report «Geochemistry of zirconium» read at the Conference on pegmatite and rare element deposits of the Ukrainian SSR (Kiev, spring of 1939) that zirconium might appear in minerals both as cation and anion.

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*GEOCHEMISTRY*

# ON THE ISOTOPIC COMPOSITION OF THE WATER OF SOME SEAS AND SALT LAKES

By I. A. KASSATKINA and K. P. FLORENSKY

*(Communicated by W. I. Vernadsky, Member of the Academy, 26. X. 1940)*

The density of the water of different seas ranges from $+0.8$ to $+2.9$ γ ([1–5]); that of the Arctic seas is somewhat higher and attains $+3.5$ γ ([6]). The isotopic composition is known only for the water of the Arctic seas ([6]).

The present authors used a combined method for determination of the density of water with a float and of the refractive index with an interferometer, as mentioned in one of the previous works of the Biogeochemical laboratory ([7]). The accuracy of the determination of density is $\pm 0.2$ γ; the error in a separate determination of the isotopes D and $O^{18}$ slightly exceeds 1 γ.

Isotopic Composition of the Water of Some Seas and Salt Lakes

| Place of sampling | Depth in m | % D | % $O^{18}$ | $\frac{\Delta d}{D\gamma}$ | $\frac{\Delta d}{O^{18}\gamma}$ | $\Sigma\Delta d$ |
|---|---|---|---|---|---|---|
| Barents Sea, 35 miles off the shore, opposite Dalne-Zelenetsky bay. 20 VIII. 1938. «Academician Baer» | 0 | −26.8 | +4.75 | −5.2 | +9.6 | +4.4 |
| Sea of Japan, near island «Russky» | 0 | + 4.8 | +0.7 | +0.9 | +1.5 | +2.4 |
| Black Sea. Sebastopol bay. Nov. 15, 1937. «Hydrograph» | 0 | + 5.2 | +1.4 | +1.0 | +2.3 | +3.3 |
| Black Sea, 43°10′ N. lat. 35°45′ E. long. Nov. 15, 1937. «Hydrograph» | 1700 | −13.7 | +3.6 | −2.6 | +5.9 | +3.3 |
| Caspian Sea, 38°52′ N. lat., 51°32′ E. long. 1933. «Sextant» | 0 | + 6.3 | 0 | +1.1 | 0 | +1.1 |
| Aral Sea, 5 km south of cape Izendy-Aral on Kulandy peninsula. Nov. 9, 1937 | 0.7 | −40.0 | +4.8 | −7.6 | +9.9 | +2.3 |

The authors' data lead to the following suggestions which are to be checked and treated in more detail after sufficient material will have been collected.

The density of the water of the Barents Sea was found to be a rather high one, the isotopic composition being characterized by a high content of $O^{18}$ and a deficiency of D. The waters of the Sea of Japan and of the Black Sea show densities usual for the sea, and an isotopic composition, approaching the

theoretical composition of sea water calculated on the basis of the process of evaporation ([5]).

The bottom water of the Black Sea has the same total density as the surface water, but essentially differs from it in the isotopic composition. The specific nature of the gaseous regime of the Black Sea and the Mediterranean origin of the bottom water do not so far permit to draw any conclusions from the above difference.

The regime of the largest salt lakes of the world—the Caspian and the Aral—makes them in many respects similar to real seas. Their isotopic composition is sharply different. Particular attention should be paid to the question of a possible connexion between the isotopic composition of the Aral and its glacier feeding, which the authors think probable on the ground of a study of the processes of thawing and freezing ([7],[8]).

The water of Kara-bogaz-gol has a density which is much above the normal, owing to the strong evaporation in this gulf. The fact that the density almost entirely depends on $O^{18}$, makes us think of the existence of some additional factor, influencing the isotopic composition. The periodical precipitation of crystalline hydrates of mirabillite may possibly be of particular importance. This question requires special study.

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*GEOLOGY*

# THE PALEOZOIC IN THE NORTHERN PART OF THE NEAR-ARAL REGION

By V. A. VAKHRAMEEV and A. L. YANSHIN

*(Communicated by A. N. Zavaritsky, Member of the Academy, 9. I. 1941)*

In autumn 1939 in the course of the geological work conducted in the northern part of the near-Aral region, the authors detected outcrops of the Paleozoic located 33 km south-westward from the town of Irghiz. These outcrops are of the greatest interest in view of their location 130 km eastwards from Mugodzhar in the central part of a region which is regarded as a deep meridional downwarping of recent Tertiary sediments. Not only has the Paleozoic been unknown here, but it could even not be supposed in the light of the ideas which dominated previously with regard to the tectonical structure of the northern part of the near-Aral region ([1],[3]). And it is only after A. L. Yanshin ([6]) had established the flat folding of the Mesozoic and Cenozoic developed here, that the appearance of the Paleozoic on the geological map became possible and consistent.

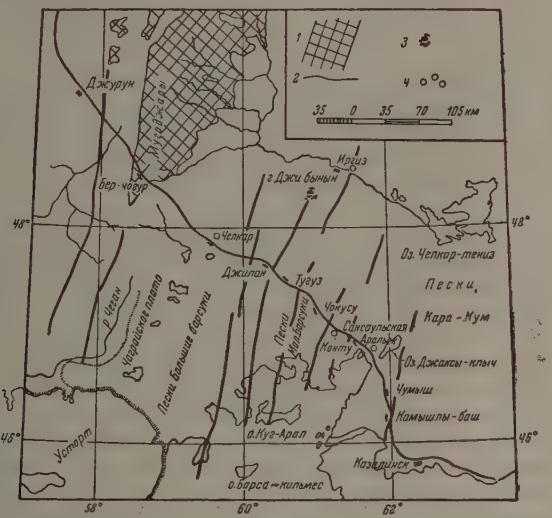
The deep bore-holes made in the synclines of the near-Aral region do not reach down to the surface of the Paleozoic. Bore-hole No. 3 at the Chelkar station has been stopped at a depth of 455 m by marine sediments of the Senonian. A bore-hole at the station of Saksaul has reached at a depth of 506 m continental Lower-Cretaceous deposits. In the intermediary anticlines, however, the Paleozoic seems to lie nearer to the surface.

The greatest (from the vertical range of its uplift) anticline of the northern near-Aral region intersects the railroad line between the stations of Djilan and Tuguz. Southwards from the line in the core of the anticline deep horizons of continental Lower Cretaceous crop out to the surface at absolute marks of 200—210 m. The outcrops of the Paleozoic detected by us are located at the northern continuation of this anticline, which we call the Tuguz anticline.

It is to be noted that they are found not in the zone of the maximum uplift of the anticline axis, but in the zone of its subsidence. Correspondingly, the projections of the Paleozoic are surrounded not by deposits of the lowermost horizons of the continental Mesozoic, as it might be expected from the existing idea of a complete peneplanation of the Paleozoic relief previous to the beginning of deposition of younger beds, but by marine sediments of the Middle Eocene (Saksaul series), resting against the Paleozoic projection. Such relations allow us to admit the existence of a buried erosional relief of the Paleozoic base of the near-Aral region and to presume

that the Mesozoic continental deposits have not been accumulated throughout the region, but only in the extensive depressions between the projections of this base. The outcrops of the Paleozoic found by the authors are without any doubt erosional remains of the ancient relief, though their appearance at the present surface is due to recent tectonical movements. In the synclines even such erosional monad rocks are buried at a considerable depth.

In the relief the Paleozoic outcrops under description form several groups of typical small hills known to the local population under the name of the Dzhibynyn-tau mountains. The Paleozoic outcrops are surrounded and




Scheme of distribution of the Paleozoic rocks of Dzhibynyn-tau among the tectonical structures of the northern part of the near-Aral region. *1*—the Mugodzhar Paleozoic, *2*—axes of Mezo-Cenozoic anticlines, *3*—the Paleozoic of Dzhibynyn-tau, *4*—deep bore-holes.

overlain by Tertiary deposits, having been freed from under the mantle of the latter only by Quaternary erosion. Bands of Tertiary sediments subdivide the Paleozoic massif into six separate spots with a total area of about 35 km². Along the margins of these more extensive spots there are found numerous individual hills and hillocks covered with Paleogene sediments.

The Paleozoic rocks exposed are subdivided into two complexes according to their composition. The more intensely metamorphozed and obviously older complex composes the two north-eastern as well as the extreme south-eastern projections of the Paleozoic. Green, epidotized, actinolitic chlorite schists are developed here, probably resulting from a metamorphization of basic effusives and their tuffs; grey, sericitic-siliceous and black chiastolitic clayey-siliceous shales, in places pierced by numerous quartz veins, following the schistosity. Individual hillocks among these rocks are composed of compact yellow silicified carbonatized serpentines; thin-sections of the latter show that they are highly talcose, contain relict grains of chromspinelides and have a relict knitted structure (the thin-sections were examined by I. F. Trusova).

The shales form minute, contorted closed folds, a background against which it is difficult to detect any large-scale structures because of the limited size of the areas of exposure. Owing to a considerable contortion, the

strike of the shales is not uniform at different points, but as a rule a north-north-east strike is predominant.

In comparing the above complex with the Mugodzhar section, described by G. I. Vodorezov in his unpublished report, it is easy to see its similarity to the Lower Paleozoic beds of this mountainous massif, composed chiefly of chloritic, phyllitic and argillaceous-chloritic shales. The time of formation of the shaly Mugodzhar complex has been somewhat arbitrarily referred by Vodorezov to the interval from the beginning of the Cambrian to the Upper Silurian.

The second, less metamorphosed and evidently younger complex of Paleozoic rocks, composing the south-western part of the small-hill area of Dzhibynyn-tau, is usually represented by epidotized tuffaceous conglomerates and tuffaceous sandstones, containing horizons of greenish-grey and reddish augitic porphyrites, and occasionally of diabases. The tuffaceous conglomerates are composed of confused fragments of porphyrites and quartz porphyres. Less frequently are encountered fragments and pebbles of red jaspers and light-grey crystalline limestones. These reach sometimes 10—20 cm in diameter.

The volcanogene complex is remarkable for its total absence of quartz veins so numerous in the older shale complex. The possibility is not excluded that the penetration of quartz veins took place before the effusion of porphyrites and the formation of tuffaceous conglomerates. Among the latter rocks outcrops of silicified serpentines are also absent.

Owing to poor exposures it proved impossible to retrace the character of the dislocations of the volcanogene complex. The tuffaceous conglomerates and porphyrites usually form only alluvial deposits at the slopes of the hills; and it is but rarely that small primary outcrops are encountered at the summits of the hills. Besides, the massif structure of the conglomerates and porphyrites prevents to detect their lamination. The volcanogene complex most closely resembles the Lower and Middle Devonian beds of the Mugodzhar range.

Of interest are the relations of the Paleozoic projections Dzhibynyn-tau with the surrounding Tertiary deposits. The latter are represented by arenaceous light-grey clays of the upper half of the Middle Eocene (Saksaul series) and by the continental Oligocene overlying these. The intermediary thick series of Chegan clays (Upper Eocene—Lower Oligocene) is absent from these sections, as it is absent from the entire arch of the Tuguz anticline. It had probably been destroyed by erosion before the deposition of the continental sediments of the Oligocene. Only by following the section of the Paleogene along the elevations westwards and south-eastwards from Dzhibynyn-tau, the appearance and gradual thickening of this series may be observed.

While approaching the Paleozoic small-hill area Dzhibynyn-tau, the rocks of the Saksaul series (Middle Eocene) and the continental Oligocene show a marked uplift of about 2—3°. This uplift is largely accounted for by a primary inclined deposition of sediments at the slopes of the Paleozoic projection. The clays of the Middle Eocene, without changing their facial character, rest against the sharp slopes of the Paleozoic erosional monadrocks, fill up the hollows between these and surround many of them from all sides, without covering them. It should be assumed that the Middle Eocene sea, whose levelling and abrading action seems to have been almost negligible, had completely or almost completely flooded the erosional Dzhibynyn-tau, which formed on the bottom an archipelago of flooded reefs. Only the highest of them were probably rising above the water as small islands.

Sideway from the massif the Paleozoic rocks are rapidly submerged under Middle Eocene sediments, composing the surrounding plain.

The continental Oligocene deposits, represented here by clays and sands with bands of ferrugineous sandstones and conglomerates, are lying on a level with the summits of the Paleozoic projections, covering up many of these. Once they had probably covered the whole of the Dzhibynyn-tau area except a few summits. Even now at the elevated plateau north of the large Paleozoic massifs one can distinctly see small isolated hillocks, composed of Paleozoic rock, to project above the almost horizontal sediments of the continental Oligocene. In places where the Oligocene mantle is carried off by erosion, the areas of Paleozoic outcrop become immediately larger.

In conclusion we should mention ([4]) the results of boring carried out in 1913 by the Immigrant Service near Lake Kara-kul 40—50 km southeastwards from the town of Irghiz at the left-hand bank of the Irghiz river. Under the clays of the Lower Eocene (Tas-Aranian series) and a small packet of the continental Mesozoic, at a depth of 57 m this bore-hole cut into micaceous shales with quartz veins and at a depth of 60.10 m it penetrated diorites down to 67.70 m. We believe it to be located at the axis of the anticline, proceeding eastwards from the Tuguz anticline, rather than at the flat-dipping bank with a NW strike, issuing from the Kara-tau mountains, as it has been supposed by Petrushevsky ([5]).

Thus, we see that the buried Paleozoic base in the north near-Aral region shows a considerable raggedness of the relief; in the anticlines, which owing to late dislocations had developed a Hercynian tectonic plan, it approaches the surface and sometimes protrudes above it.

Judging by the recent papers by Bykov ([2]) and Levenson (oral information), similar modes of occurrence of Paleozoic rocks are observed in more northern parts of the Aral-Turgai lowland, at the upper course of the Abuga river and at the watershed between the latter and the Ulkoyak river. These circumstances are to be given full attention when conducting artesian test-boring and in prognosticating the search for buried coal basins, the existence of which in the synclines of the Aral-Turgai lowland is very probable.

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*GEOLOGY*

# MARINE SEDIMENTS AT THE WATERSHED BETWEEN THE TOSNO AND SABLINKA RIVERS

By E. A. ANSBERG and O. M. ZNAMENSKAYA

*(Communicated by V. A. Obruchev, Member of the Academy, 2. I. 1941)*

In summer 1940 the Sablino educational research station of the Leningrad State University undertook in the vicinity of Sablino, south the glint line in the Leningrad region, detailed prospecting work involving boring and levelling, with the object of studying both the history of development of the relief and the Quaternary deposits of the Tosno river basin (O. M. Znamenskaya) and the ground water hydrology of the adjoining watersheds (E. A. Ansberg). As a result of this work a very interesting material was collected. Particular attention belongs to the finding of intermoraine marine deposits at the watershed between the Tosno and Sablinka rivers (E. A. Ansberg).

The intermoraine deposits have been exposed by two adjoining bore-holes, Nos. 42 and 43, along the profile intersecting the watershed of the Tosno and Sablinka rivers from the village of Maloye Ghertovo to that of Kozlovka, somewhat upstream from the latter. Both bore-holes have been sunk at the highest points of the watershed of the given profile with an absolute mark of their mouth +35 m. The distance between these bore-holes is 120 m. The more complete section of one of the bore-holes (No. 43) is given below in descending order:

1) Vegetative stratum.

2) Loam containing no bowlders, light-brown with thin bands of grey sands below (type of ribboned deposits).

3) Brown loam, compact, with ferrigineous spots and small quantity of crystalline rock bowlders.

4) Loam with rare bowlders, light, compact, bluish-grey, in the open air changing colour to a lighter one.

5) Fine-grained sand, bluish-grey, thinly laminated.

6) Loam without bowlders, grey, thinly laminated with bands of white sand.

7) Compact clay, greyish-black, in the open air losing colour, thinly laminated. At some depth from the surface of these clays there have been found fragments of shells; the lower portion of the beds contains small worn crystalline bowlders.

8) Medium-grained sand, slightly argillaceous.

9) Brownish-green loam, very compact, argillaceous, coarse, with an abundance of small chiefly crystalline bowlders.

10) Lower Silurian limestones.

This section shows that the marine sediments, with fragments of shells are overlain by beds, composed of deposits containing no bowlders, and an upper moraine; these are overlain by a moraine-like loam which O. M. Znamenskaya considers to be a lower moraine.

At the base of the adjoining bore-hole No. 42 the moraine-like loams (lower moraine) are absent, being evidently eroded, and the marine sediments are lying directly upon country rock under the upper moraine. The fragments of shells discovered in the intermoraine clays of the bore-hole No. 42 were found to be *Portlandia*, *Yoltia arctica* and *Tellina calcarea* (according to a preliminary determination made by A. J. Lesnikova, and a later detailed study by M. A. Lavrova), which points to the marine origin of the intermoraine formations.

A preliminary examination of a number of samples of marine clays for pollen showed that the upper horizons of the marine beds are rich in pollen of thermophylic species (hazel-wood up to 25% and occasionally hornbeam). The quantity of the pollen of thermophylic species in marine sediments, when compared with the occurrence of thermophylic species at the present time, makes us conclude that the climatic conditions had been milder than those prevailing now.

Along the line of this profile bore-hole No. 41, the nearest to bore-hole No. 42 in the direction of the Tosno river, stands 250 m apart. Marine intermoraine sediments are absent here. The nearest bore-hole No. 44 in the direction of the Sablinka river, is located at a distance of 180 m from No. 43. Intermoraine sediments have not been found here either. The marine formations at the elevated portions of the ancient relief have evidently been eroded or swept away by a redescending glacier, which deposited the upper moraine. Of interest is the regular shift of facies of marine sediments in both adjoining bore-holes (Nos. 43 and 42); below sand; above compact thin clay; still higher up argillaceous bands alternating with arenaceous ones and, finally, sands lying on the top in bore-hole No. 43. Such a facial variability observed in the two adjoining bore-holes points to a gradual deepening of the basin at the beginning and a shallowing at the end of its existence. The regular alternation of facies as well as the finding of marine deposits in the hollow of the preglacial relief is evidence in favour of a primary occurrence of marine formations. In the vicinity of Leningrad marine sediments overlain by moraines have been known since 1921 at the Mga river near the station of Gora within the Neva depression (N. V. Potulova). These deposits have been studied by a number of investigators (N. V. Potulova, I. M. Pokrovskaya, Kotlukov, Skorokhod, G. Brander, S. A. Yakovlev and others); so far, however, there is no agreement on their stratigraphical position and age.

The marine intermoraine deposits discovered at the Silurian plateau are analogous to those at the Mga river, both from the fauna discovered and their general habit. This should be taken to mean that the sea basin which deposited the clays with *Yoltia arctica* and *Tellina calcarea* had been covering the Silurian plateau with absolute marks above 32 m (top horizon of marine formations at the Silurian plateau). Consequently, V. L. Menaker (1940) was wrong in considering the glint as a formation produced purely by abrasion; nor is it reasonable to trace along it the presumptive shore-line of the basin under description, which should have passed much to the South from the glint.

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*MINERALOGY*

# NEW CONCEPTION OF THE TERM «HARDNESS»

By M. I. KOIFMAN

*(Communicated by A. F. Joffe, Member of the Academy, 6. XII. 1940)*

The conception of hardness and the methods for measuring the latter have been developed long since. In spite of the numerous experimental and theoretical investigations and the great practical importance of the problem in different fields of science and technics, the essence of the concept of «hardness» is still lacking sufficient clearness. Many authors have pointed to the unsatisfactory status of ideas as to the physical sense of this conception and emphasized the difficulty of the investigations of the problem.

In mineralogical sciences hardness is often determined as a resistance to scratch and abrasion of small particles from the surface layers ([1–6]).

In metallophysics and technology of metals hardness is usually defined as resistance to penetration with foreign bodies (ball, cone, pyramid, etc.). It is also defined as the energy of surface dispersion ([7]). In discussing a number of methods for the measurements of brittle bodies Kuznetzov ([8]) proposes to discard (for these methods) the very conception of «hardness», replacing it by that of «strength» and «surface energy».

For lack of clear and precise ideas as to the essence of hardness, the papers devoted to the study of rational measurement problems and to the relation of hardness to other physical properties of solids abound in contradictions. The principal vice of all the definitions is that they do not cover the conception of hardness completely and thoroughly, but only partly, one-sidedly. Besides, in none of the existing formulations is hardness opposed with sufficient sharpness to another allied conception, that of «mechanical strength».

Because of their one-sided character, the definitions mostly include but a part of the methods of measurement, the methods of measurement of brittle or plastic bodies. The definition of hardness as the energy of surface dispersion and an equivalent of surface energy does not include all the methods of testing bodies in a state of plasticity. At the same time all the formulations widely spread in the technology of metals exclude all the methods connected with surface dispersion. The definition of hardness as the resistance to scratch, abrasion etc. is used in a still narrower sense.

It is quite clear, however, that the conception of hardness as a definite property cannot depend on the peculiar features of one or another group of bodies. The conception of hardness must be unified.

In spite of the abundance of methods of measurement, the diversity of objects pursued by the authors working in different fields and propounding different principles, devices and modifications of apparatus for measuring the hardness of different bodies, it is always possible, however, to establish one feature in common: in all cases of measurements of hardness different means are being used locally to affect the surface layers of the

objects under test. The most characteristic distinction of all the methods of hardness measurement is the small area of the surface or the volume, within which the activity of the agent and the consequences of agression are concentrated. The static and dynamic mechanical strain applied in hardness tests is always concentrated within a small area of the surface of the body. A localization of the injury is distinctive both of the methods of hardness determination and of all the devices used for this purpose without any exception. The localization of the aggressive strain produces a partial destruction or deformation, the nature and the amount of which depends on the mechanical properties of the object, the peculiarities and intensity of the external strain or on the amount of energy applied, as well as on the continuance of the influence exercised by the aggressive agents.

A focussed strain of considerable intensity may produce a complete crushing or deformation of the whole body. Under certain conditions, however, it results only in a local deformation or local breakage. Deformation takes place in the case when the body is in a state of plasticity, breakage—when it is brittle. Partial breakage and plastic deformation in the zone of agression represent, however, only two kinds of local mechanical trauma.

Hence the new formulation of the conception. Hardness is a resistance of the surface layers of the body to local injury (breakage or deformation) under the influence of mechanical strains, concentrated within a limited area of the body. More concisely, the conception of hardness may be defined as a local resistance to concentrated mechanical aggression or local mechanical resistance.

From the new definition follows a difference between the conception of hardness and that of strength. While the latter characterizes the resistance of the whole body to complete destruction (shearing, breakage, crushing) or general deformation under the influence of external mechanical strain, hardness should be regarded as the resistance of the surface layers of a body to a local effect of strains insufficient to produce complete crushing, but resulting in a local injury within a certain area.

Like the general conception of «strength», the idea of hardness must also be differentiated into a range of particular conceptions, characterizing definite kinds of hardness according to the character and conditions of the local breakage. Every kind of hardness will have not only its own particular sense, but will possess also a definite practical significance. These peculiar kinds in turn may be further differentiated with regard to shape and size of the destructive tools, the intensity of external forces, etc.

Consequently, hardness is a complex conception. It may be static and dynamic as well, and it may characterize the resistance to normal strains (indentation, etc.) or combined tangential-normal (scratch, grinding, cutting, etc.). Resistance to concentrated strains may be measured either by the amount of stresses producing local injuries of definite intensity, or by the energy applied to produce deformation or to uncover a new surface.

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*MINERALOGY*

# ON A FINDING OF VEINS OF NATIVE ARSENIC NEAR GUTAY VILLAGE OF THE CHITA DISTRICT

By N. TOLKACHEVSKA

*(Communicated by A. E. Fersman, Member of the Academy, 15. I. 1941)*

Two veins of pure native arsenic (analysis of the laboratory of the Zapokrovsk arsenic mine, 1939) were struck in spring of 1938 when sinking the pit No. 3 (for molybdenite) on the left bank of the river Chikoy opposite to the molybdenite mine. They were found to run under rather unusual conditions and, though cannot be said to have any but a purely mineralogical importance, it is worth while nevertheless to describe their occurrence.

Previous investigations showed the region of the Chikoy (Gutay) molybdenum deposit to be built up of the most ancient primary sedimentary bed, referred to the Archean ere, which under contact action of plutonites was totally converted into gneisses and crystalline shales, injected lit-par-lit by granite which is close to diorite; as a result of this injection ribbon and augen-gneisses were formed. A bed of these rocks forming in the region under consideration an anticlinal fold of the ESE strike, is compressed inbetween two granite massifs, one of which is located on the left bank at a distance of about 0.5 km from the pit No. 3; the contact dips pitward. Molybdenoferous quartz veins striking NW 320—333° and dipping NE at an average angle of 45° occur in the bed of amphibolites, in the northern limb of the anticline, on the right bank of the river Chikoy. The left bank of the river within boundaries of the mine represents the southern anticlinal limb and is overlain by thick terrace depositions of the Chikoy river. Data obtained as a result of sinking pits show the section of these deposits to be as follows: under a vegetation cover there occur very pure river sands slightly cemented by an argillaceous material and containing practically no pebbles Lower in sands are encountered argillaceous partings and separate large well-rounded pebbles up to 30 cm in diameter. Further there occur continuous absolutely uncemented pebble beds containing a small amount of coarse-grained sand. Under the pebble bed abruptly begin strongly weathered, coated by an ochreous film amphibolites, along whose slips thin (up to 10 mm) veinlets of molybdenite are observed. Intercalations of light-coloured greenish-grey, strongly quartzitified cherts up to 1 m in thickness are encountered in the amphibolite. The contact of cherts with amphibolites is very sharp, but nothing marks it specially. Thin (0.95—0.5 mm) veinlets of pyrite crystals are met with in slips of amphibolites and cherts as well. There the

pyrite is much lighter in colour than in the main body. At the depth of 15—18 m the pit pierced a zone of dislocation about 40 cm in thickness filled by a strongly ochreous material ground to argillaceous state; still lower the pit passed through very dense amphibolites, which are strongly injected by granite with abundant pyritization in slips and sometimes with thin intercalations of light-coloured cherts.

The vein of native arsenic was struck at the depth of 9—10 m first in the NW pit wall. The vein dips SW at an angle 20—25°; its thickness is in average about 6—7 cm with swells up to 17 cm. The second vein of native arsenic, which in no way differs from the first one, was struck 1.15 m lower. Both veins rest in amphibolites which are much lighter in colour and pierced by numerous strings of calcite several mm thick. Both are confined to the tectonic zone, being, thus, the result of filling dislocation fissures by a native arsenic of shelly concentric structure with thin (only several mm in thickness) vein walls of calcite. It was supposed that by sinking a cross-cut from the pit at the depth of 20 m along the azimuth 205—225° the arsenic vein would be undercut. This supposition, however, was not justified as the cross-cut pierced from the very beginning amphibolites strongly injected by granite and showing molybdenite and pyrite on their slips. The cross-cut traversed, moreover, a band of thin quartz-carbonate strings, striking NW and dipping NE, which contained numerous inclusions of light-coloured pyrite. Beautiful crystals of calcite were encountered in voids of one of the veins of this band. On the 51 m the cross-cut struck a sheeted body of very dense, light-grey, strongly mineralized quartzite about 3 m in thickness; this body abounds in minute dust-like grains of light-coloured (arsenicous ?) pyrite and arsenicous yellowish ochre. Further the cross-cut passed through dense amphibolites absolutely identical to those observed on the right bank of the Chikoy river and enclosing quartz molybdenoferous veins.

Spectral analysis of the native arsenic carried out at the laboratory of the Geological Institute of the Academy of Sciences (the analyst S. L. Borovick) showed strong lines of arsenic and antimony, lines of copper (above average), traces of chromium, average lines of calcium, traces of aluminium and, finally, very weak lines of magnesium, silicon and iron to be present.

Chikoy Mine
of Rare Metals.

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*BIOCHEMIE*

# ÜBER DIE ZUSAMMENSETZUNG DES ÖLES AUS DER RINDE DER LINDE *(T. PARVIFOLIA)*

Von A. A. SOLNZEW

*(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 11. IV. 1940)*

Auf die Ablagerung von Öl in der Rinde überwinternder Bäume wurde erstmals von A. S. Famintzin und I. P. Borodin hingewiesen. Späterhin wurde diese Frage von einer Reihe von Forschern untersucht. Für die Charakteriserung des Öls und die Untersuchung des ölbildenden Vorganges in den lebenden Zellen der überwinternden Bäume wurden gewöhnlich entweder die anatomische Analyse oder die Bestimmung der physikalisch-chemischen Eigenschaften des Öls, wie z. B. spezifisches Gewicht, Brechungsindex und Jodzahl, herangezogen. Wir haben die Zusammensetzung des aus der Rinde der Linde (*T. parvifolia*) stammenden Pflanzenöles genauer analysiert, worüber in vorliegender Mitteilung berichtet wird.

Die Rinde junger Linden wurde im Februar gesammelt. Vor der Extraktion wurde die Rinde zwei Wochen lang bei Zimmertemperatur, dann in Thermostaten im $CO_2$-Strom bis zu einem Feuchtigkeitsgehalt von 5.7% getrocknet. Die Extraktion wurde mit Petroläther (Fraktion 45—65°) durchgeführt. Die Ausbeute an Öl, auf trockene Rinde berechnet, betrug 8%. Die physikalisch-chemischen Eigenschaften des Öles aus Lindenrinde sind in Tabelle 1 angeführt.

Tabelle 1

| Spez. Gewicht bei 20° | Brechungsindex bei 22° | Säurezahl | Verseifungszahl | Jodzahl |
|---|---|---|---|---|
| 0.956 | 1.4808 | 9.6 | 197 | 96.59 |

Die Verseifung des Öles wurde mit einer alkoholischen Lösung von KOH im Wasserstoffstrom ausgeführt. Nach der Bearbeitung der Seifenlösung mit Petroläther wurde 9.23% (auf die Ölmenge berechnet) Unverseifbares erhalten. Das Unverseifbare ist ein kristallines schwach orange gefärbtes Produkt. Nach dem ersten Umkristallisieren aus Alkohol fielen aus der Mutterlauge ziemlich gross und regelmässig ausgebildete Kristalle vom Schmelzpunkt 133° aus.

Die Hauptmenge aber wurde nach mehrfacher Kristallisation, zuletzt aus absolutem Alkohol, fein-kristallin erhalten; S. P. 182—183°. Die Acetylprobe ergab in der Hauptsache den Gehalt an Phytosterin. Der Schmelzpunkt des Acetats war 161—165°. Der Gehalt an grösseren Mengen Phytosterin

konnte durch die Hager-Salkowskys, sowie Liebermann'sche Reaktion ebenfalls bestätigt werden. Die Elementaranalyse des Phytosterins vom Schmelzpunkt 182.5° zeigte:

| | | | |
|---|---|---|---|
| C—84.38% | | C—84.40% | |
| H—11.57% | was der Formel | H—11.55% | d.Theorie |
| O— 4.05% | $C_{28}H_{48}O$ entspricht | | |

Phytosterin von derartigen Zusammensetzung und Schmelzpunkt ist offensichtlich ein spezifisches Stoff der Lindenrinde, denn in der Analyse der Fette ist dieser bisher noch nicht beschrieben worden.

Die Zerlegung der Seifen und die Abscheidung der Fettsäuren wurde wie üblich ausgeführt. Bei der Vakuumdestillation konnten etwa 2% flüchtiger Säuren isoliert werden. Eine nähere Bestimmung dieser Säuren gelang nicht wegen Mangel an Substanz. Mit Hilfe der üblichen qualitativen Methoden konnte festgestellt werden, dass die erwähnten Säuren ein Molekulargewicht besitzen, das über demjenigen der Propionsäure liegt. Die physikalisch-chemischen Eigenschaften der Fettsäure sind in Tabelle 2 angeführt.

Tabelle 2

| Spez. Gewicht bei 20° | Brechungsindex bei 22° | Neutralizationszahl | Jodzahl |
|---|---|---|---|
| 0.949 | 1.4723 | 208 | 96.8 |

Die Trennung der gesättigten von den ungesättigten Säuren wurde nach Twitchell ausgeführt. Es muss hierbei bemerkt werden, dass beim Auflösen der Säuren in heissem Alkohol und bei der Zugabe einer heissen Lösung von Bleiacetat, ebenso bei der nachfolgenden Bromierung der ungesättigten Säuren, eine teilweise Verharzung eintritt.

| | | |
|---|---|---|
| Gesättigte Säuren—4.8% | | |
| Palmitinsäure —3.7% | Schmelzpunkt des | |
| Stearinsäure —1.4% | Säuregemisches—4.7° | |

Die isolierten ungesättigten Säuren besitzen folgende chemische Eigenschaften:

| | |
|---|---|
| Jodzahl | —102 |
| Neutralizationszahl | —204 |
| Molekulargewicht | —270 |
| Oleinsäure | —ca 52% |
| α-Linolsäure | — 43% |

Bei der Trennung der Bromide der ungesättigten Säuren konnte kein Hexabromid festgestellt werden, dagegen wurde eine geringe Menge (etwa 1%) des Oktobromids erhalten, das nur in heissem Benzen löslich war. Der Schmelzpunkt dieses Bromids betrug ohne Umkristallisation 185—187°. Beim Schmelzen färbt sich das Bromid dunkel. Wegen der geringen Menge konnte der Bromgehalt nach Carrius nicht bestimmt werden.

Der Zusammensetzung nach kann das aus Lindenrinde erhaltene Öl zu den halbtrocknenden Ölen gezählt werden.

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*GENETICS*

# ON THE RÔLE AND NATURE OF THE *Y*-CHROMOSOME IN MALES OF *DROSOPHILA BUSCKI*

By J. D. KRIVSHENKO

*(Communicated by I. I. Schmalhausen, Member of the Academy, 20. IX. 1940)*

Data on the non-disjunction of the sex chromosomes in various species of *Drosophila* (*melanogaster*, *simulans*, *virilis*, *ananassae*) show that among primary exceptions there occur both females (*XXY*) and males (*XO*), the latter being as a rule more frequent. According to the cumulative data of Bridges (1916), Safir and Mevor (1925), the ratio existing between male and female exceptions, obtained as the result of primary non-disjunction in females of *D. melanogaster*, amounts to about 1 : 4; according to the summed up data of Kikkava (1932—1935), Arau (1930), Demerec and Farrow (1930) this ratio equals 1 : 7, while according to Kikkava it amounts to 1 : 15.

Our studies of primary and secondary non-disjunction of the sex chromosomes in males and females of *D. buscki* have shown that exceptional *XO* males are totally lacking in the given *Drosophila* species. Out of the 85469 flies examined, obtained as a result of the crosses carried out for the study of primary non-disjunction in males and females, 73 exceptional females have been found, while exceptional males have not been detected.

On the basis of experimental data and the mechanism of reduction division which is responsible for the appearance of corresponding exceptional types, one would conclude that the absence of *XO* exceptional males in *D. buscki* may be due to the fact that either the gametes (*O*-eggs, or *O*-sperms) which lack the sex chromosome, or the zygotes of the *XO* type, perish.

According to Muller and Settles (1925), Kühn (1929) and others, the gametes with variously aberrant chromosome complexes usually survive in *D. melanogaster*. In view of this, one may assume that in *D. buscki*, too, the absence of *XO* males is caused by the destruction of corresponding zygotes, rather than of the gametes of the *O* type. However, for lack of data confirming this assumption as applied to a new species with some specific peculiarities (Krivshenko, 1939), we refrained from drawing final conclusions and decided to find out experimentally why the *XO*-chromosome structure is absent just in *D. buscki*. Is it because the gametes of the *O* type perish immediately after reduction division, or else because later on, after fertilization, the zygotes of the *XO* type, showing a deficiency in one sex chromosome, perish in the course of individual development?

No exhaustive answer to this question can be given, unless such experimental conditions are created under which the gametes of the *O* type of the one

sex will meet the $XY$ or $XX$, instead of the $X$ gametes, the latter combination yielding the $XO$ zygotes. This fertilization will completely reestablish the normal chromosome complex (in the former case—the complex of the male, in the latter case—that of the female) of the zygote. Therefore, if only the gametes of the $O$ type really do survive, such zygotes will necessarily be produced.

Without dwelling on the details of the method, we shall only note that for the experiment we used females of the $XXY$-chromosome structure, whose $Y$-chromosome bore the dominant *Gap* gene and the $X$-chromosome—the gene *vermilion*. Such females lay about 50% eggs of the $XY$ type. The $Y$-chromosome of $XY$ males used for this experiment bears the dominant gene *Carved**, while the $X$-chromosome bears the gene *concave* (Krivshenko, 1939). According to preliminary data, in the males of the given mutant line the gametes of the $O$ type are formed at a frequency of about 0.23%. Therefore, about 0.11% of $X^{v}\ Y^{Ga}$ males should be expected in the progeny of the $X^{v}X^{v}Y^{Ga}$ females crossed with $X^{cc}\ Y^{Crd}$ males produced from the fertilization of $XY$ eggs with $O$ sperms. Table 1 shows the results of this cross.

Table 1

Results of Crossing $X^{v}X^{v}Y^{Ga}$ Females with $X^{cc}\ Y^{Crd}$ Males

| Females | | | | | | Males | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| Normal | | | | Exceptional | | Normal | | | Exceptional | |
| *normal* | *Gap* | *Carved* | *Carved—Gap* | *vermilion—Carved* | *vermilion* | *vermilion—Carved* | *vermilion—Carved—Gap* | *vermilion—Gap* | *concave—Gap* | |
| 942 | 777 | 4 | 2 | 2 | 1 | 926 | 706 | 1 | 3 | 3360 |

In Table 1 the most interesting are classes six and nine. The examination of each separate chromosome has shown that the flies of those classes are due to fertilization with the sperm of the $O$ type; in the former case $X^{v}\ X^{v}$ eggs were fertilized, in the latter one—$X^{v}Y^{Ga}$ eggs. Eggs of the $X^{v}X^{v}$ type are layed in very small numbers and the occurrence of a female of the *vermilion* phenotype ($X^{v}X^{v}O$) was due to our good fortune, indeed. As mentioned above, the $X^{v}\ Y^{Ga}$ eggs are layed in great numbers (about 50%) and, therefore, the occurrence of a $X^{v}\ Y^{Ga}$ male, i. e. of the *vermilion—Gap* phenotype, was to be expected. The analysis of these flies according to their progeny confirmed the assumption as to their structure and origin.

The data on the structure and origin of the female of class six and of the male of class nine point to that in *D. buscki* the sperm of the $O$ structure is viable and does not lose its fertilizing power in the case the $X$- or the $Y$-chromosome is absent.

Similar results have been obtained on the viability of the eggs of the $O$ type.

Table 2 gives the results of crosses between $X^{w}\overset{\frown}{X^{w}Y^{Ga}}$** females and $X+Y^{Ga}Y$

* The $Y$-chromosomes bearing the *Gap* and *Carved* genes represent reciprocal translocations between the $Y$- and III$L$-chromosomes. The dominant characters *Gap* and *Carved* are closely linked with the $Y$-chromosome in their inheritance.

** The arches above the $X$ and $Y$ chromosomes in these females indicate the genetic connexion between these chromosomes which becomes manifested during inheritance. No cytological connexion has been found. The $\overset{\frown}{X^{w}Y^{Ga}}Y$ males do not survive.

males. According to the data of our preceding work, the females used in this experiment produce in great numbers eggs of the *O* type. The males of the given chromosome structure produce spe ms of the types *XY* and $XY^{Ga}$ in about equal ratio.

Table 2

Results of Crossing $X^{w}\overset{\frown}{X^{w}Y^{Ga}}$ with $X^{+}Y^{Ga}Y$

| Females | | | Males | | | | Total |
|---|---|---|---|---|---|---|---|
| *normal* | *Gap* | *white—Gap* | *white* | *white—Gap* | *normal* | *Gap* | |
| 855 | 1204 | 3 | 190 | 254 | 2 | 2 | 3175 |

The males of classes six and seven in Table 2 are evidently due to fertilization of eggs of the *O* type with *XY* sperm in the former case, and with $XY^{Ga}$ sperm in the latter. The analysis of these males according to their progeny confirmed their assumed origin and chromosome structure.

The fact that the gametes of the *O* type (*O*-eggs and *O*-sperm) are viable and possess fertilizing power, makes it reasonable to expect the formation of zygotes of the *XO* type, and, consequently, leads to the possible occurrence of corresponding forms of imago. As a matter of fact, despite the abundant material obtained by us on primary non-disjunction, no such individuals have ever been observed. This seems to be due to the fact that the absence of an *Y*-chromosome in the zygote of the *XO* type has a negative effect on the processes of individual development, this causing its destruction.

According to numerous data obtained during the study of primary non-disjunction of the sex chromosomes in other *Drosophila* species, the imago males of the *XO* structure are viable and do not differ from males of a normal chromosome structure, i. e. from *XY* males, except for being sterile. The conclusion to be drawn is that here the *Y*-chromosome is genetically comparatively void, and plays no rôle in the formation and viability of male individuals.

*D. buscki* males of the *XO* chromosome structure do not occur. This seems to be accounted for by the fact that the *Y*-chromosome, being an indispensable element of the male chromosome complex of this *Drosophila* species, contains genes which cause the form-building processes and viability as a whole. Such an interpretation of the rôle played by the *Y*-chromosome of *D. buscki* has so far never been applied to any of the studied *Drosophila* species; in the light of the evolution of the sex chromosome it is also of considerable interest.

Nowadays most of geneticists believe that the *Y*-chromosome of *D. melanogaster*, being genetically empty, is a degeneration product of a formerly genetically valuable chromosome, possibly homologous with the *X*-chromosome (Neuhaus, 1938). All the data on the rôle played by the *Y*-chromosome in the processes of reduction division of individual development and on the viability of the individuals bearing this chromosome in hypo- or hyperploid condition, go to confirm this assumption.

It should be noted that the above conception as to the origin of the *Y*-chromosome is based exclusively on the final result of the evolution process,

i. e. on the degenerated chromosome. No intermediate stages have been observed which might confirm the probability of this conception. The *Y*-chromosome of *D. buscki* is possibly that lacking intermediate element. Those processes which took place in the evolution of the *X*-chromosome in *D. melanogaster* did not go so far as those in *D. buscki*. Therefore, the *Y*-chromosome of *D. buscki* has remained a genetically important element of the male chromosome complex, necessary for the development of the zygote.

The following data seem to support this assumption. 1) On the cytological preparations of the salivary gland nuclei, the *Y*-chromosome of *D. buscki* is a clearly organized component equal to about $^1/_{24}$ of the length of the *X*-chromosome (Krivshenko, 1939). 2) The male zygotes survive, given the presence of an insignificant proximal region of the *Y*-chromosome (although the viability of these males is greatly reduced). 3) The preliminary data of E. D. Gaponova show that *normal* allels of the *X*-chromosome genes are present in the *Y*-chromosome of this *Drosophila* species. These data convincingly show the homology existing between the *X*- and *Y*-chromosomes. Successful experiments carried out on the homology of the *X*- and *Y*-chromosomes will decidedly give a firm genetic experimental basis for explaining the nature and the origin of the *Y*-chromosome and will at the same time serve as material for understanding the evolution of the sex chromosomes.

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*PLANT PHYSIOLOGY*

# COLD-RESISTANCE OF WHEAT $F_2$ HYBRIDS WITH REFERENCE TO PHASIC CHARACTERISTICS OF THEIR PARENTS

By E. SAPRYGUINA

*(Communicated by A. A. Richter, Member of the Academy, 2. I. 1941)*

Inheritance of cold-resistance by plants has been the subject of a quite considerable number of papers. Some authors found it to display a transgressive nature, surpassing the parent in both directions ([1], [2]) or yielding more resistant forms ([3],[4]). Others obtained intermediate forms ([6]), sometimes with an extremely wide range of fluctuations from one parent to another ([7]), and which had their acquired quality now as a dominant ([8]), now as a recessive character ([9–12]). Others again observed various types of inheritance in $F_1$ ranging from dominant to recessive, according to the components involved ([5], [13]), the intensity of cold-treatment ([14]) and the conditions of growing the young hybrid plants ([15]). But in none of the works on the transmission of cold-resistance by descent has there ever been established the relation between the type of inheritance and the physiological properties of the varieties crossed, although some attempts to clear up this point have been made ([2], [16]). And as long as this relation remained unknown, it was not possible in studying hybrids for cold-resistance to tell what type of segregation in $F_2$ might be expected from a given pair of parents, nor to select the components properly in order to produce more resistant forms. But then came the theory of phasic development ([17–19]) to show the importance of the vernalization phase ([20–23]) and, later on, also of the light phase for the winter-hardiness of plants ([24–27]). It was possible now to base the study of cold-resistance on varieties with known phasic characteristics and not on chance material. Saltykovsky ([29–31]) was the first to show how the resistance of hybrids to cold is affected by the length of the above phases in their parents. In the present paper, too, the cold-resistance of $F_2$ hybrids will be considered in relation to the phasic characteristics of their parents.

Phasic Development and Cold-Resistance of Parents. The hybrids studied had been obtained by crossing different biotypes of spring and winter wheats selected by the method of phasic analysis, according to T. D. Lyssenko ([32]). All spring wheats involved had a very short phase of vernalization. As for their light phase, they were increasingly late in the order: Prelude (Canada), 25183 (Afghanistan), 841 (Krasny Kut), 48/02 (Saratov), 274 (Odessa), 4952 (Sweden), 3483 (Finland), 321 (Omsk). The winter wheats used in crossing can be characterized as follows (Table 1).

Table 1

| Variety | Length of the vernalization phase (approximate fig.) | Length of the light phase | Cold-resistance |
|---|---|---|---|
| 3060/15 (selected from the wheats of Azerbaidjan) . . . . . | 15 days | very short | ranges from extremely low to very strong in the same order |
| 534 (Azerbaidjan) . . | 40 » | short | |
| Kooperatorka (Odessa) | 45 » | medium | |
| Ukrainka (Mironovka) | 50 » | » | |
| *Hostianum* 237 (Saratov) . . . . . | 55 » | long | |
| *Lutescens* 329 (Saratov) . . . . . | 60—65 » | very long | |
| Bg 4 (Bezenchuk) . . | 60—65 » | » » | |
| Bg 21 (Bezenchuk) . | 60—65 » | » » | |

Table 2

Survival Ratio (in %) among $F_2$ Hybrids Wintering in the Field

| Components ♀ | Components ♂ | Normal snow cover ♀ | Normal snow cover $F_2$ | Normal snow cover ♂ | Deeper cover ♀ | Deeper cover $F_2$ | Deeper cover ♂ | Date of earing of spring parents planted April 26, 1936 |
|---|---|---|---|---|---|---|---|---|
| | | | | 1936/1937 | | | | |
| Prelude | × 534 | — | — | — | 0 | 0 | 3 | June 10 |
| 274 | × 534 | — | — | — | 0 | 2 | 4 | » 19 |
| 3483 | × 534 | 0 | 2 | 3 | 0 | 6 | 4 | » 22 |
| 321 | × 534 | 0 | 3 | 4 | 4 | 10 | 3 | » 30 |
| Prelude | × Kooperatorka | — | — | — | 0 | 4 | 98 | » 10 |
| 841 | × » | 0 | 10 | 72 | 0 | 21 | 98 | » 14 |
| 274 | × » | 0 | 16 | 72 | 0 | 23 | 98 | » 19 |
| 4952 | × » | 0 | 25 | 74 | 0 | 43 | 94 | » 22 |
| 3483 | × » | 0 | 22 | 95 | 0 | 47 | 98 | » 22 |
| 321 | × » | 0 | 56 | 90 | 4 | 75 | 98 | » 30 |
| Prelude | × 329 | — | — | — | 0 | 9 | 100 | » 10 |
| 841 | × 329 | 0 | 26 | 100 | 0 | 26 | 100 | » 14 |
| 25183 | × Bg4 | 0 | 16 | 96 | 0 | 21 | 100 | » 9 |
| 48/02 | × Bg4 | 0 | 28 | 96 | 0 | 29 | 100 | » 17 |
| 321 | × Bg21 | 0 | 93 | 100 | 2 | 94 | 100 | » 30 |
| | | | | 1937/1938 | | | | |
| 841 | × Kooperatorka | 0 | 5 | 53 | 0 | 60 | 96 | |
| 274 | × » | 0 | 8 | 53 | 0 | 65 | 96 | |
| 3483 | × » | 0 | 14 | 62 | 67 | 93 | 96 | |
| 321 | × » | 0 | 21 | 62 | 83 | 93 | 89 | |
| 3060/15 | × » | 0 | 16 | 85 | 36 | 84 | 96 | |
| 321 | × 3060/15 | 0 | 0 | 0 | 78 | 60 | 20 | |
| 841 | × 329 | 0 | 15 | 95 | 0 | 75 | 97 | |
| 274 | × 329 | 0 | 22 | 95 | 2 | 71 | 97 | |
| 321 | × Bg21 | 0 | 57 | 96 | 76 | 90 | 99 | |
| 3060/15 | × 329 | 0 | 24 | 93 | 57 | 85 | 95 | |
| 534 | × 329 | 1 | 49 | 92 | 84 | 93 | 97 | |
| Kooperatorka | × 329 | 49 | 87 | 92 | 92 | 97 | 97 | |
| Ukrainka | × 329 | 86 | 90 | 91 | 91 | 95 | 95 | |
| 237 | × Bg4 | 96 | 97 | 95 | 96 | 98 | 100 | |

Determination of Cold-Resistance. The hybrids were tested for cold-resistance at the Bezenchuk experimental station in 1936/1937 and in 1937/1938. In the first year the determinations were carried on in the field only, but in the second year they were carried on both in the field and at the laboratory. Planting in the field was done in quadruplicate, each set containing 250 grains. On either side of a hybrid set the parent sets were planted, 125 grains in each. To secure different degrees of cooling two of the sets were allowed to pass winter under the natural cover of snow, while for the two other a deep snow cover was created in the middle of winter. The laboratory determinations of cold-resistance were made according to the method described previously ([33],[34]).

The data obtained have shown that the formation of cold-resistant forms among wheat hybrids is based on two developmental phases of their parents: the vernalization phase and the light phase. This is especially conspicuous in the following three groups of crosses.

The first group includes hybrids obtained by crossing a series of spring wheats widely varying in the length of their light phase with a winter wheat variety. Such hybrids form a regular series, in which their cold-resistance increases with the length of the light phase of their spring parents. This rule will be observed always, no matter which of the winter wheats is chosen as the other component of the cross. It may be variety 534 as well, as Kooperatorka, or Bg 21, or 329. With Kooperatorka in the field experiment of 1936/1937 the survival ratio among the hybrids kept under the thick cover of snow varied from 4 to 75%, according to the length of the spring parent light phase. In the case of more resistant winter parents the survival ratio under similar conditions ranged between 9 and 94%. Under the natural cover of snow a greater proportion of hybrid plants had been killed, but the above order of cold-resistance was even more obvious, as is shown by the figures in Table 2.

No less plainly is it brought out by the data of laboratory tests, summarized in Table 3.

Table 3

Survival Ratio among $F_2$ Hybrids in the Laboratory Test of 1937/1938

| Components | —17°C | | | —19°C | | | —24°C | | | With ice crust —23°C | | | —27°C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ♀ ♂ | ♀ | $F_2$ | ♂ | ♀ | $F_2$ | ♂ | ♀ | $F_2$ | ♂ | ♀ | $F_2$ | ♂ | ♀ | $F_2$ | ♂ |
| 274 × Kooperatorka | 0 | 14 | 60 | 0 | 11 | 53 | — | — | — | — | — | — | — | — | — |
| 321 × » | 0 | 34 | 62 | 0 | 25 | 58 | 0 | 18 | 50 | 0 | 9 | 37 | — | — | — |
| 841 × 329 | 0 | 17 | 96 | 0 | 17 | 88 | 0 | 5 | 90 | — | — | — | — | — | — |
| 274 × 329 | 0 | 25 | 92 | 0 | 25 | 85 | 0 | 10 | 92 | — | — | — | — | — | — |
| 321 × Bg21 | 0 | 50 | 89 | 0 | 45 | 85 | 0 | 19 | 89 | 0 | 2 | 74 | — | — | — |
| 3060/15 × 329 | 0 | 44 | 100 | 0 | 39 | 88 | 0 | 19 | 89 | 0 | 4 | 77 | — | — | — |
| 534 × 329 | 28 | 51 | 100 | 21 | 50 | 89 | 0 | 21 | 92 | 0 | 8 | 77 | 0 | 1 | 79 |
| Kooperatorka × 329 | 33 | 83 | 100 | 25 | 77 | 98 | 10 | 41 | 88 | 8 | 38 | 79 | 0 | 9 | 77 |
| Ukrainka × 329 | 88 | 93 | 100 | 41 | 89 | 93 | 20 | 86 | 88 | 9 | 70 | 76 | 3 | 68 | 78 |

In the second group belong hybrids from any of the spring varieties crossed in succession with a series of winter varieties of increasingly long developmental phases. Such hybrids will prove the more resistant, the longer the two developmental phases of their winter parents. In 1937/1938 among the hybrids from 321 × Bg21, 321 × Kooperatorka and from 321 × 3060/15 the survival rate under natural snow cover was 57, 21 and 0% respectively (Table 2). In 1936/1937 the results had been similar.

Under the third group are classed hybrids between the extreme types of wheats. Their first parent has one of its phases (either the vernalization phase, or the light phase) long, the other short. Their second parent has both its phases long. $F_2$ hybrids from such crosses show very little variation as regards frost-resistance. In the freezing experiments of 1936/1937 the survival rates among such hybrids were as follows:

| | —17°C | —19°C | —24°C |
|---|---|---|---|
| $F_2$ 534 × 329 . . . . . | 51 | 50 | 21 |
| $F_2$ 321 × Bg 21 . . . . | 50 | 45 | 19 |

In the field the results were similar.

So we arrive at the conclusion that even with a small set of parent varieties crossed in various combinations it is possible under equal external conditions to obtain $F_2$ hybrids showing all recorded types of cold-resistance. But it is possible only when the main physiological types of wheat are properly crossed in pairs, according to their phasic characteristics.

Every combination will yield hybrids which, subjected together with the parents to varying degrees of cold, will show varying rates of survival even if the more resistant of the parents has survived completely and the other has completely perished. From this one may conclude that the hybrids segregating out in $F_2$ will range from one parent to another through a continuous series of increasingly frost-resistant forms.

As the frost-resistance of hybrids depends strongly upon two developmental phases of their parents, transgressive forms more resistant to cold than the parents can be easily obtained among them. Segregation in hybrid progenies with respect to cold-resistance can be foretold before crossing, when the phasic characteristics of the parents are known.

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*PLANT PHYSIOLOGY*

# GROWTH RESPONSE OF SOYA TO DAYLENGTH IN RELATION TO DEVELOPMENT

By G. M. PSAREV and Kh. A. VESELOVSKAYA

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In spite of considerable progress in the domain of growth physiology, it must still be realized that the growth of an adult plant, its inner rhythm and the external factors involved are not sufficiently investigated. This is especially true of the problem which invites now our closest attention and that is, what are the relations in plants between growth and development.

According to the views which had won a temporary recognition in physiological literature, growth, or the vegetative activity of plants, was believed to be opposed to development, or to their reproductive activity ([1]). Thus, the relation appeared to be an antagonistic nature ([2]). But these views have no longer any credit to-day. However, as the question of what is the essence and physiological nature of the developmental process has now become the object of persistent attacks, there has also grown up the necessity of exploring more fully the physiological side of the correlations existing between the processes of growth and development.

Indeed, it is largely because our knowledge of these correlations is in unsettled condition, that so essentially different views have been expressed on the sexual development of plants ([4–6]). This is also the source of the disagreement concerning the influence of external factors (vernalization, photoperiods) on growth processes.

While some of the authors credit vernalization with a positive influence on plant growth ([7–9]), others consider it as a negative factor ([10]). With regard to photoperiods the most widespread opinion among the investigators is that growth is depressed by short and stimulated by long days. Recently this relation in the growth response was confirmed by some data on perennial plants ([11]) and accounted for by a respective regularity in the formation of growth hormones ([12]).

But, on the other hand, there have been noted some facts which point to a positive influence of short daylengths on the growth of plants in general ([13]) and, for certain plants, also on their increase in thickness ([14]) and the cambial growth of their stems ([15]). It will therefore be obvious that the relations here are by far not so simple as was supposed by some of the authors.

To approach the problem more closely was the object of our experiments of which but a small part, all referring to a single culture, the soya, are reported in the present paper. They were started in 1936 and involved a rather wide range of varieties of different geographical origin. The plants were grown in an open ground on small plots on varying daylengths. Curtailing the daily period of light was effected by screening the plots with knitted cotton fabric of a dark colour, stretched over wooden frames. On the other

hand, when daylengths were to be made longer, electric light was applied in addition to natural light. The data on the time of flowering, as obtained in those tests, are partly set forth in Table 1.

Table 1

Number of Days from Germination until the Outset of Flowering with Reference to Daylength

| Variety and year | Origin | Photoperiodic conditions | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Natural day | 3 short followed by natural | 5 short followed by natural | 8 short followed by natural | 10 short followed by natural | 15 short followed by natural | short (10 hour) day throughout |
| Local North-Caucasian, 1939 | Unknown | 36.80 | 29.90 | 29.30 | 28.50 | 29.20 | 29.90 | 29.50 |
| Krushul 9/3, 1939 | Manchuria | 36.10 | 31.90 | 32.20 | 32.30 | 31.70 | 29.90 | 30.20 |
| Kharbin 231-a, 1939 | » | 44.60 | 32.50 | 30.30 | 30.50 | 29.40 | 29.60 | 26.60 |
| Pure line 03768—Kharbin 118, 1939 | » | 44.40 | 33.30 | 30.70 | 30.90 | 29.80 | 28.80 | 28.50 |
| Pure line 08807—Kharbin 111, 1939 | » | 47.00 | 33.20 | 31.80 | 30.00 | 29.50 | 30.00 | 28.80 |
| Illiny, 1939 | America | 64.60 | 33.10 | 30.50 | 27.50 | 28.00 | 26.40 | 26.50 |
| Catalogue No. 9398, 1939 | Japan | 43.50 | 35.60 | 33.10 | 29.90 | 31.70 | 30.20 | 29.80 |
| Catalogue No. 9400, 1939 | » | 62.30 | 33.00 | 32.00 | 27.50 | 27.40 | 26.20 | 26.20 |
| Catalogue No. 12871, 1938 | » | 61.10 | 40.12 | 33.70 | 27.70 | 26.60 | 26.00 | 25.60 |
| Chinese Turkestan, 1937 | China | 69.20 | — | 38.40 | — | 35.70 | 33.90 | 32.40 |
| Catalogue No. 12078, 1938 | India | 81.20 | — | — | 29.90 | 30.60 | 30.90 | 29.00 |
| Catalogue No. 12076, 1939 | » | 45.00 | 32.50 | 30.90 | 28.60 | 29.00 | 28.90 | 28.00 |

In Table 1 every group is seen to be composed of forms whose reproductive activity is not equally affected by the same photoperiodic conditions. So much so, in fact, that the difference between the groups is reduced to a wider or narrower range of variation which the form they include show with regard to the length of the period preceding the outset of flowering. Neither is there any great difference between the groups in respect to the number of short days required from the very start to bring the plants sooner to flowering. This number varied from 3 to 10 in most of the cases.

The growth response of the plants is brought out by the figures of Table 2.

Increase in height is seen to vary according to the number of short days. Unless this number exceeds a certain limit, the effect of short photoperiods is to stimulate growth. But if the limit has been passed, a depression of growth will take place. The depression sets in abruptly in some varieties and more smoothly in others. While 3 to 5 short days suffice to call it forth in some cases, in others 5 to 8, and in others again 10 or even more short days are required.

So there seems to be a particular threshold in the growth reaction of every variety to increasing accumulation of short photoperiods in the early phase of development. And when the plant is thus made to increase in height, it does so not only by increasing the number of nodes, but its internodes grow longer, too.

This threshold form of photoperiodic response becomes also apparent when other aspects of growth are considered. It is observed, for instance, in the rhythm of growth when increase in height is followed up across separate periods of development.

The above data allow us to make the following generalizations:

1. The results of our observations on the development and growth within a wide range of soya varieties have revealed the existence of re-

gular and simultaneous changes in the processes of development and growth, which, in its turs, points to the existence in the plant of a close physiological contact and correlation between the phenomena of growth and development.

2. Every set of varieties within a geographical group shows a different responsiveness to the daylength with regard to the outset of flowering; the differences observed between the groups are expressed in a more or less wide range of variation of the reproductive activity of the plant.

3. There is a threshold in the increase of height in soya in response to daylength and the outset of an abrupt, or milder depression of growth corresponds to a definite number of short days received by the plant at the start of its development. Those numbers of short days which approach the threshold appear usually to stimulate the growth of the plant.

4. The described changes in the process of growth are reflected in the number of nodes and in the length of internodes, in other words, both the factor of development and that of growth are involved.

The results obtained give ground to believe that the effect of curtailing the daylength is to increase the accumulation of growth substances in plant tissues, rather than to decrease it. And when a depression of growth is called

Table 2

Height of Main Stem and Average Internode Length (in cm) as Affected by Daylength

| Variety | Photoperiodic conditions | | | | | | |
|---|---|---|---|---|---|---|---|
| | Natural day | 3 short followed by natural | 5 short followed by natural | 8 short followed by natural | 10 short followed by natural | 15 short followed by natural | Short (10-hour) day throughout |
| Local North-Caucasian | | | | | | | |
| Height | 60.20 | 25,00 | 27.70 | 17.10 | 19.20 | 15.30 | 10.94 |
| Internode length | 4.30 | 3.06 | 2.79 | 2.26 | 2.60 | 2.03 | 1.52 |
| Krushul 9/3 | | | | | | | |
| Height | 65.55 | 69.23 | 69.33 | 67.22 | 62.50 | 40.20 | 16.95 |
| Internode length | 4.48 | 4.84 | 4.70 | 4.48 | 4.02 | 3.06 | 1.62 |
| Kharbin 231-a | | | | | | | |
| Height | 92.50 | 95.40 | 101.60 | 93.44 | 79.07 | 35.95 | 14.20 |
| Internode length | 5.25 | 5.08 | 5.19 | 4.76 | 4.21 | 3.50 | 1.49 |
| Pure line 03768 | | | | | | | |
| Height | 89.20 | 90.10 | 94.30 | 88.11 | 87.44 | 40.06 | 14.80 |
| Internode length | 5.05 | 5.10 | 5.43 | 4.95 | 4.64 | 3.31 | 1.53 |
| Pure line 08807 | | | | | | | |
| Height | 85.10 | 100.20 | 98.20 | 39.10 | 31.80 | 20.80 | 15.00 |
| Internode length | 4.74 | 5.48 | 5.31 | 4.23 | 3.16 | 3.47 | 1.73 |
| Illiny: Height | 103.30 | 130.22 | 115.70 | 40.62 | 38.20 | 27.50 | 15.22 |
| Internode length | 5.09 | 6.11 | 5.43 | 4.08 | 3.89 | 3.12 | 1.65 |
| No. 9398: Height | 43.90 | 24.40 | 22.70 | 19.00 | 19.81 | 21.06 | 14.72 |
| Internode length | 3.38 | 2.81 | 2.91 | 2.58 | 2.60 | 2.95 | 1.86 |
| No. 9400: Height | 102.40 | 106.30 | 27.00 | 25.60 | 21.90 | 19.75 | 16.56 |
| Internode length | 5.11 | 5.33 | 3.33 | 3.69 | 2.86 | 2.67 | 2.06 |
| No.012871: Height | 73.60 | 61.30 | 24.50 | 23.60 | 20.81 | 15.90 | 12.93 |
| Internode length | 3.56 | 3.47 | 3.47 | 3.05 | 2.83 | 2.01 | 1.70 |
| Chinese Turkestan | | | | | | | |
| Height | 92.12 | — | 22.40 | — | 17.70 | 16.40 | 12.44 |
| Internode length | 4.57 | — | 2.55 | — | 2.71 | 2.04 | 1.51 |
| No. 12078: Height | 86.75 | 72.00 | 75.00 | 35.12 | 31.50 | 20.75 | 15.37 |
| Internode length | 4.53 | 3.71 | 3.77 | 3.03 | 3.31 | 2.33 | 1.87 |
| No. 12076: Height | 2.55 | 106.55 | 109.00 | 94.30 | 86.20 | 48.25 | 21.70 |
| Internode length | 5.42 | 5.73 | 5.80 | 5.18 | 4.97 | 4.15 | 2.06 |

forth by too many short days, it may be accounted for either by too high a store of growth substances, or by an abnormal proportion of some of them in the complex which they all build up.

6. The varieties and populations within each soya group are characterized by a quite definite activity as regards their growth response to daylength, namely: a) the Manchurian group shows mostly a low, less frequently an intermediate activity in the manifestation of threshold changes; b) the Japan group, on the contrary, displays a high, less frequently an intermediate activity; c) to judge from some data refferring to 1940, representatives of the China group show all three kinds of threshold changes of growth. As for the Indian group, we dispose of no sufficient data to characterize its growth response to daylength.

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*PFLANZENBIOLOGIE*

# DIE BESTÄUBUNG VON *TARAXACUM KOK-SAGHYZ* ROD. BEI PLANTAGEBEDINGUNGEN

Von M. S. GHILAROV

*(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 16. X. 1940)*

Die Untersuchung der Bestäubung von Kok-saghyz bei natürlichen Bedingungen in dem Kegenbezirk (Semiretschje), die von F. N. Prawdin ausgeführt wurde, hat gezeigt, dass trotzdem Kok-saghyz von den Bienen scheinbar nicht oft besucht wird, letztere doch die häufigsten Besucher (verschiedene Halictusarten) der blühenden Körbchen darstellen; sie übertragen den Blütenstaub von Pflanze zu Pflanze und sichern die Fremdbestäubung. Bei Einführung der Kultur von Kok-saghyz in umfangreichem Masstabe und der Entwicklung der Samengewinnung dieser Kautschukpflanze, war es notwendig aufzuklären, in wie weit die Plantagen von Kok-saghyz durch Insektenbestäuber versorgt sind, denn davon hängt auch der Samenertrag der sich fremdbestäubenden Pflanzen ab.

Die Untersuchung wurde an zweijährigen Plantagen von Kok-saghyz in der Kautschukwirtschaft No. 17 (bei Kursk) durchgeführt. Die Feldarbeit wurde gemeinsam mit der Laborantin G. P. Moissejewa ausgeführt. An der Bearbeitung des Materials beteiligte sich F. N. Prawdin, welcher die Methode der Zählung der Bestäuber vorschlug.

Arbeitsmethode. Die Zählung der Insekten, die die blühenden Körbchen von Kok-saghyz besuchen, wurde in folgender Weise vorgenommen. Inmitten einer blühenden Plantage (100 ha Fläche) wurde eine kleine Zählparzelle von 100 m² abgeteilt, die 3 Reihen der Saat von Kok-saghyz umfasste. Am Tage vor Beginn der Zählung wurden auf der Parzelle 200 noch nicht blühende, aber am folgenden Tag zum Öffnen bereite Körbchen mit Gazestreifen markiert. Während des Blühens der markierten Körbchen (4—5 Tage) wurden auf der Parzelle täglich blühende Körbchen und jede Stunde alle Besucher der blühenden Körbchen gezählt. Die Bestimmung wurde mit einer Genauigkeit, wie sie die Zählung in gewisser Entfernung ermöglichte, vorgenommen. Zur Kontrolle der Bestimmung wurden nebenbei die Besucher der blühenden Körbchen in den Insektenvertilger gesammelt. Man berechnete die mittlere Zahl der Besucher der blühenden Körbchen auf 100 m² Fläche und auf 1000 blühende Körbchen. Letzteres war deshalb notwendig, weil die Zahl der auf der Parzelle blühenden Körbchen an verschiedenen Tagen variierte. Der Vergleich der Anzahl der Besucher, die nach der Methode von Prawdin, nach Angaben von gleichzeitig auf 3 Zählungsparzellen durchgeführten Zählungen, bestimmt wurden, beweist die Genauigkeit dieser Methode.

Nach Beendigung des Blühens der markierten Körbchen, wurden sie, um ein Zerfliegen der Samen zu verhindern, mit Stoffisolatoren bedeckt. Die

Bestimmung des Ausfüllungsgrades wurde mittels durchfühlen aller gesammelten Früchte mit der Präpariernadel vorgenommen. Ihre Keimfähigkeit wurde in dem Laboratorium für Samenkontrolle nach der üblichen Standardmethode bestimmt.

Wie die in der Periode vom 11—26 Juni ausgeführten Bestimmungen gezeigt haben, in dem Komplex der Besucher der blühenden Körbchen des 2-jährigen Kok-saghyz in Kursk betrug die Menge der Insekten, die die Fremdbestäubung sichern (Bienen, Fliegen und Schmetterlinge), 34.4% der Besucher (933 von 2712), Insekten, die zufällig Bestäuber sein können (parasitäre *Hymenoptera*, Ameisen, Käfer *Olibrus* und *Euspermophagus* usw.), 52.14% und schliesslich 13.46% Insekten, die die Blütenkörbchen beschädigen (Käfer *Meloidae*, *Cantharis* usw., verschiedene Wanzen). Unter den Bestäubern haben die Bienen (69.35%) die grösste Bedeutung. Die Bestimmung von 370 Bienen, die in den Vertilger während der Zeit vom 9. VI bis 5. VII gesammelt worden waren, zeigte, dass 70.3% von der Gesamtmenge der gesammelten Bienen, den Hausbienen angehörten. Die wilden Bienen waren durch folgende Gattungen vertreten: *Halictus* 28.3%, *Andrena* 0.8%, *Melitta* 0.3%, und *Sphecodes* 0.3%.

Somit sind die Hausbiene und die Halictusarten die Hauptbestäuber von Kok-saghyz. Die Beobachtungen über die Bienentätigkeit auf Kok-saghyz haben gezeigt, dass die kleinen Arten (*Halictus* spp.) den Blütenstaub, die grossen Arten (Hausbiene, *Andrena*) Nektar nehmen. Fliegen und Schmetterlinge besuchen Kok-saghyz ebenfalls wegen des Nektars.

Die Zählungen der Besuche des Kok-saghyz durch die Bestäuber wurden bei verschiedenen meteorologischen Bedingungen ausgeführt. Diese Zählungen haben gezeigt, dass die Aktivität der Bestäuber, ihre Anzahl auf der Plantage, und das Verhältnis zwischen den verschiedenen Gruppen sich in Abhängigkeit von den Witterungsverhältnissen merklich ändert, vor allem von der Lufttemperatur. Die Gesamtzahl der Insekten, welche die Körbchen von Kok-saghyz auf der gegebenen Fläche besuchen, steht in mehr oder weniger direkter Abhängigkeit von der mittleren Lufttemperatur. In den Tagen der niedrigsten Temperatur (etwa 13°) war die Anzahl minimal, in den Tagen der höchsten (23—24°)—maximal.

Es ist bemerkenswert, dass die beständigsten Besucher der Körbchen von Kok-saghyz, die bei jeder Witterung erscheinen, die Käfer *Olibrus bicolor* F. sind Insekten, die mit der Gattung *Taraxacum* biologisch eng verbunden sind (die Larven von *O. bicolor* entwickeln sich in den Samenkörbchen von Kok-saghyz).

Noch auffallender tritt der Einfluss der Temperatur auf die Sättigung der Plantage mit den Hauptbestäubern—den Bienen—hervor. Die Anzahl der auf dem Felde tätigen Bienen, die auf die gegebene Menge blühender Körbchen fällt, befindet sich in direkter Abhängigkeit von der Lufttemperatur. Bei mittlerer Tagestemperatur unter 17° vermindert sich der Besuch des Kok-saghyz durch die Bienen—sowie die wilden, als auch die Hausbienen—auffallend; an besonders kalten und nebligen Tagen aber (bei einer mittleren Temperatur von 13—15°) stellen die Bienen auf Kok-saghyz ihre Arbeit vollständig ein.

In Abhängigkeit von den Witterungsverhältnissen ändert sich nicht nur die Gesamtanzahl der Bestäuber, sondern auch das prozentuale Verhältnis der einzelnen Gruppen. Bei mittleren Lufttemperaturen höher als 17° herrschen in dem Komplex der Bestäuber die Bienen vor, während bei niedrigen Temperaturen—die Fliegen vorherrschen. Die Rolle der Fliegen als Bestäuber ist viel weniger bedeutend, als diejenige der Bienen. Der schlechtere Besuch des Kok-saghyz durch die Bestäuber an kalten und nebligen Tagen wird in gewissem Grade dadurch kompensiert, dass bei

diesen Bedingungen die Pflanzen länger blühen, und die Körbchen während längerer Zeit der Bestäubung zugänglich sind. Unter wolkenlosen Himmel dauert das Blühen des Körbchens 4 Tage; das Körbchen bleibt offen während 24—28 Stunden. Bei trübem Wetter beträgt die Blütenperiode 5 Tage und das Körbchen ist offen während 40—50 Stunden.

Von der Parzelle mit markierten Körbchen, die während der Bestimmung der Sättigung der Plantage durch Bestäuber blühten, wurden Samen zur Untersuchung der Abhängigkeit ihrer Ausfüllung von dem Besuche der Körbchen durch die Bestäuber gesammelt. An jedem der drei Zählungsfristen wurden je 200 Körbchen genommen, und die Füllung der gesammelten Früchte bestimmt. Bei verschiedenen Bedingungen des Besuchs war der Samenansatz fast gleich.

Wird die Bestäubung von Kok-saghyz durch die minimale Menge der bei den Zählungen beobachteten Bestäuber gesichert? Die minimale Durchschnittsmenge der Bienen, die bei den Zählungen beobachtet wurden, war 0.7 auf 1000 blühende Körbchen (16—20. VI). Das Blühen der Körbchen dauerte während dieser Periode 5 Tage, die Tätigkeit der Bienen—etwa 5 Stunden täglich. Somit betrug die Arbeitszeit, während welcher die Bienen Kok-saghyz bestäuben konnten, 1500 Min., d. h. die Arbeitszeit der Bienen betrug auf 1000 Körbchen 1050 Bienen-Minuten (0.7 Bienen$\times$1500 Min.).

Spezielle chronometrische Beobachtungen haben gezeigt, dass im Durchschnitt während 1 Min. die Hausbiene 64.3$\pm$2.7% Blütchen in den Körbchen von Kok-saghyz besucht, d. h. dass die Biene zur Bestäubung jedes Körbchens gegen 80 Sek. braucht. Wenn wir diese Leistung als Durchschnittsleistung für die Biene annehmen, finden wir, dass die Bienen in der Periode der minimalen Besuchszahl des Kok-saghyz durch die Bestäuber die Bestäubung von 787 Körbchen von 1000, d. h. 78.7%, sicherten. Es muss in Betracht gezogen werden, dass die Leistung der Bestäubungstätigkeit der Biene auf Grund der Zählung der Blütchen in den Körbchen von Kok-saghyz bestimmt wurde, aus denen die Hausbiene während 1 Zeiteinheit den Nektar säugt (durchschnittlich aus einem Blütchen in 1 Sek.). In Wirklichkeit aber ist die Bestäubungsarbeit der Bienen höher.

Wenn wir diesen Umstand, sowie das Vorhandensein von anderen Gruppen von Bestäubern, wie Fliegen, die in dieser Zeit die Bienen an Zahl sogar übertreffen, berücksichtigen, muss man zugeben, dass auch in Perioden der minimalen Besuchszahl des Kok-saghyz durch die Bestäuber seine Bestäubung in Kursk region gesichert war.

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*PFLANZENMORPHOLOGIE*

# NEUE EXPERIMENTELL ERHALTENE HYBRIDFORMEN DER EICHEN: ×*QUERCUS MICZURINII* UND ×*QUERCUS WYSSOTZKYI*

Von S. S. PJATNITZKY

*(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 29. XII. 1940)*

In der Literatur ([1],[2],[3]) sind über 80 Artbastarden der Eichen, die durch natürliche Kreuzung in der freien Natur entstanden sind, beschrieben. Die Mehrzahl dieser Hybriden ist durch Kreuzung, ihrer systematischen Stellung nach, nahe verwandter Arten entstanden; es kommen aber auch Hybriden vor bei Arten, die verschiedenen Sektionen der Gattung *Quercus* angehören. Besonders selten sind Hybriden zwischen den Arten der Sektion *Erythrobalanus* und den Arten anderer Sektionen, sie kommen jedoch auch vor. So hat Sargent ([2]) einen Hybrid beschrieben, der durch natürliche Kreuzung von *Q. obtusata* (Sektion *Lepidobalanus*) mit *Q. velutina* Lamarck (Sektion *Erythrobalanus*) entstanden ist. Mit der künstlichen Hybridisierung der Eichen haben sich beschäftigt: Klotsch ([4]), der einen Hybrid von *Q. Robur* L. mit *Q. pedunculata* Ehrh. erhalten hat, und Ness ([5],[6]), der eine Kreuzung von *Q. virginiana* Mill mit *Q. lyrata* Walt., *Q. platanoides* Sudw. und *Q. minor* Sarg. vornahm. Von den von Ness erhaltenen Hybriden ist gegenwärtig schon $F_2$ gezüchtet, welche von Jarnell ([7]) beschrieben wurde.

In den Arbeiten über die Bildung von Artbastarden der Eichen, die 1937 ([8]) begonnen wurden, wurden als Stammeltern folgende Arten benutzt: *Q. Robur* L., *Q. sessilis* Ehrh., *Q. alba* L., *Q. macrocarpa* Mich., *Q. montana* Willd. (Sektion *Lepidobalanus*), *Q. macranthera* F. et M. (Sektion *Mesobalanus*), *Q. Suber* L. (Sektion *Cerris*), *Q. borealis* Mich. var. *maxima* Asch. (Sektion *Erythrobalanus*). Im ganzen wurden 43 Kreuzungskombinationen ausgeführt, über 70000 Blüten bestäubt und ungefähr 2500 Hybrideicheln erhalten.

Aus den gezüchteten Hybridpflanzen können gegenwärtig zwei Formen isoliert werden. Die erste Form ist aus der Kreuzung von *Q. macranthera* F. et M. (♀) mit *Q. borealis* Mich. var. *maxima* Asch. (♂) entstanden. Sie ist somit ein Beispiel eines entfernten Sektionsbastarden, erhalten durch Kreuzung einer Art aus der Sektion *Erythrobalanus*, die sich überhaupt schwer mit Individuen anderer Sektion der Gattung kreuzt. Diese Hybridform wurde × *Q. Miczurinii* genannt. Sie kann in folgender Weise charakterisiert werden. Dicke, mächtige Sprosse, jung nicht dicht behaart, einjährig leicht behaart oder fast kahl, grau oder oliven-grau. Die Achselknospen sind rötlich-braun, leicht behaart, zugespitzt, länglich-konisch, dem Spross angedrückt, Länge

etwa 0.5 cm; die Scheitelknospen sind bis 1.0 cm lang, konisch, ebenfalls rötlich-braun gefärbt. Die Nebenblätter sind nadelförmig, bis 0.5 cm lang, in der Mehrzahl der Fälle bleiben sie nur bei der oberen Blattrosette erhalten. Die Blätter sind kurzgestielt (0.4—0.6 mm), kompakt, lederartig, auf der oberen Seite dunkelgrün, matt, leicht rauh behaart, auf der Unterseite hellgrün oder bläulich, stark aber nicht dicht rauh behaart (besonders längs der Nerven), die Haare sind lang mit 3—4 Verzweigungen. Die Form der Blätter ist breit-reziprok-eiförmig, reziprok-eiförmig oder länglich-oval, 7—15 cm lang, 4—8 cm breit, an der Spitze mit einem kurzen dreieckigen, manchmal gezähnten, zugespitzten Lappen, an den Seiten mit 6—8 Paaren nicht vollkommen gegenständigen Lappen, spitzigen, zugespitzten oder stumpf-zugespitzten. Die Lappen sind im oberen Teil des Blattes kleiner, ganzrandig, mehr oder weniger dreieckig mit seichten ($^1/_5$—$^1/_3$ der Breite der Blattspreite) Einschnitten; die Lappen des mittleren Teiles des Blattes sind bedeutend grösser, ganzrandig oder grob gezähnt mit tieferen (bis zu $^1/_2$ der Breite der Blattspreite) Einschnitten. Bei vollkommen entwickelten Blättern im mittleren Blatteil findet sich ein tiefer Einschnitt zwischen den Lappen, der mehr als die Hälfte der Blattspreitenbreite einnimmt (die sogen. «Durchschnürung»). Die Blattbasis ist keilförmig, manchmal leicht abgerundet. Die Seitennerven treten an der Unterseite ziemlich stark hervor, die Hauptnerven führen zu den Lappenspitzen, wo sie endigen; zwischen ihnen können schwächer ausgeprägte Nerven, die nicht bis zum Rand der Blattspreite verlaufen, sondern sich mit den Verzweigungen der Hauptseitennerven verbinden, vorhanden sein.

Eine Reihe von Kennzeichen der beschriebenen Hybriden hat einen intermediären Charakter; zu solchen Kennzeichen gehören—die Form und Anzahl der Blattlappen, die Dichte seiner Behaarung und der Behaarung der Sprosse. Die anderen Kennzeichen entsprechen den Kennzeichen des einen oder des anderen der Stammeltern: so ist die Nervatur der Blätter ähnlich der Nervatur bei *Q. borealis*, die Stiellänge und Grösse der Knospen entspricht eher den Kennzeichen bei *Q. macranthera*, während die Form der Haare, der frühe Verlust und die geringe Grösse der Nebenblätter die Hybridform dem *Q. borealis* näher bringt. Jedoch entsprechen eine Reihe von Kennzeichen der Hybridform weder den Kennzeichen von *Q. macranthera* noch denjenigen von *Q. borealis*; die rauhe Behaarung z. B. ist für keine dieser Arten charakteristisch; sie ist aber bei ihren Hybriden deutlich ausgeprägt; die Knospenform untersheidet sich bei den Hybriden ebenfalls von denjenigen der Elternarten. Zu diesen «neugebildeten» Kennzeichen muss man auch das Auftreten «der Durchschnürungen» bei den oben beschriebenen Blättern der Hybridform rechnen.

Die zweite Hybridform wurde durch Kreuzung von *Q. macranthera* F. et M. (♀) mit *Q. Robur* L. (♂) erhalten. Sie wurde × *Q. Wyssotzkyi* genannt zum Andenken an meinen Lehrer G. N. Wyssotzkyi. Wir führen im folgenden die Beschreibung dieser Form an: starke Sprosse, die Jungen leicht behaart, die einjährigen fast kahl, grünlich grau, oliven-grau oder grau. Die Achselknospen braun, leicht behaart, eiförmig, stumpf oder etwas zugespitzt, dem Spross angedrückt, etwa 0.3 mm Länge; die Scheitelknospen etwas länger und mehr ausgezogen. Die Nebenblätter nadelförmig, bis zu 0.5 cm Länge, bei manchen Exemplaren bleiben sie nur bei den oberen Blättern erhalten. Die Blätter fast sitzend oder auf ganz kurzen Stielen von weniger als 0.5 cm Länge, kompakt, auf der Oberseite intensiv grün, glänzend, fast kahl oder mit einer geringen kurzen und weichen Behaarung, auf der Unterseite grünlich-blau, leicht weich behaart; die Behaarung ist kurz, die Haare meistenteils nicht verzweigt. Die Blattform ist reziprok-eiförmig, von 9—18 cm Länge, 4—8 cm Breite, an der Spitze mit einem kurzen, stumpfen,

abgerundeten Lappen, an den Seiten mit 6—8 Paaren gegenständigen oder manchmal nicht ganzgegenständigen, abgerundeten, stumpfen oder manchmal stumqf-zugespitzten Lappen. Die Lappen sind im oberen Teil des Blattes klein, mit seichten ($^1/_5$—$^1/_6$ Breite der Blattspreite) Einschnitten, ganzrandig, in dem mittleren Teil etwas grösser, mit Einschnitten bis zu $^1/_4$ Breite der Blattspreite, meistens ebenfalls ganzrandig und nur manchmal bei entwickelteren Blättern grob gezahnt. Ein tiefer Einschnitt kommt in dem mittleren Teil des Blattes nicht vor. Die Blattbasis ist herzförmig oder sogar mit mehr oder weniger entwickelten «Öhrchen», die für *Q. Robur* charakteristisch sind. Die Seitennerven springen auf der Unterseite stark hervor und sind nicht parallel. Die am stärksten entwickelten Nerven verlaufen zur Spitze der Lappen, wo sie endigen; zwischen ihnen finden sich Nerven, welche mit den Nerven dritter Ordnung, die von den Hauptseitennerven entspringen, verbunden sind. Nach ihren Kennzeichen ist dieser Hybrid eine Zwischenform zwischen beiden Stammeltern. Einige ihrer Merkmale entsprechen mehr den Kennzeichen der väterlichen als der mütterlichen Art; zu diesen Merkmalen gehört die Art der Blattnervatur und die Form der Basis der Blattspreite.

Die beschriebenen Hybridenformen sind in dem von mir gezüchteten Material durch eine beträchtliche Anzahl von Exemplaren—× *Q. Wyssotzkyi* mehr als 200 Pflanzen und × *Q. Miczurinii* gegen 15 Pflanzen—vertreten. Einzelne Pflanzen jeder der oben beschriebenen Formen variieren nach der einen oder anderen Richtung in bezug auf die oben beschriebenen Typen hinsichtlich einer Reihe von unbedeutenden Merkmalen, wie z. B. Erhaltung oder Verlust der Nebenblätter, Anzahl der Blattlappen, Farbe der Sprosse und Grösse der Knospen, aber der allgemeine Typus bei den Pflanzen, die einer bestimmten Form angehören, bleibt erhalten. Viele der Bastardpflanzen weisen einen kräftigen Wuchs auf; dieser Umstand lässt auf ihre praktische Bedeutung in der Zukunft hoffen.

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*PFLANZENANATOMIE*

# ÜBER DIE ZENTRALEN HARZGÄNGE IN DEN NADELN DER *PINUS SILVESTRIS* L.

Von M. MOISSEJEWA

*(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 18. XII. 1940)*

Die Harzgänge, welche sich im Zentralzylinder der Kiefernadel befinden, wurden offenbar schon in den 80-ger Jahren des vorigen Jahrhunderts von Engelmann entdeckt und als «zentrale» bezeichnet [zitiert nach Wettstein (1)]. Eine Reihe von Forschern entdeckte und beschrieb dieselben ebenfalls in den 80-er Jahren und auch später an zwei- und dreiblättrigen Pinusarten (2—7). 1937 werden sie durch Djaparidze (10) von neuem als Zentralgänge bezeichnet. Wenn wir aus den Untersuchungen von Mojejko (8) und Wassilewskaja (9) auch wissen, dass viele von diesen Gängen in den Zweig übergehen und auf diese Weise als Abflussbahn für das Harz dienen, so sind doch über den Anfang und Verlauf der Gänge in der Nadel, soweit mir bekannt, noch keine erschöpfenden Angaben vorhanden.

Djaparidze (10) und Wassilewskaja (9) vermuten, auf Grund ihrer Forschungen, dass die zentralen Harzgänge in dem Transfusionsgewebe in der Nähe des Xylems als eine Gruppe kleiner parenchymatischer Zellen ihren Anfang nehmen. «Bei weiterem nach abwärts gerichtetem Verlauf in der Nadel, nähern sich die Gänge allmählich dem Xylem, wobei sich ihre Struktur zugleich vervollkommnet: inmitten der locker zusammengeführten Parenchymzellen entsteht der Kanal des Ganges. An der Stelle, wo die Nadeln verschmelzen, ihre Nerven aber noch isoliert sind, haben die Gänge ein gut ausgebildetes Epithelium und einen weiten Kanal; sie treten entweder dicht an das Xylem heran oder befinden sich schon im Bereich desselben» (10), wobei diese Gänge in der Nadel von *Pinus silvestris* L. nur in ihrer unteren Hälfte beginnen und nicht mehr als zwei in jeder Nadel zu finden sind. Bei *P. hamata* (Stev.) D. Sosn., welche «einige Autoren als eine Varietät der gemeinen Kiefer, andere aber als selbstständige Art ansehen, ... erreichen die Zentralgänge die Mitte der Nadel, und die Maximalzahl derselben ist um das Doppelte höher als bei der gemeinen Kiefer» (9).

Ich hatte wiederholt die Gelegenheit bei *Pinus silvestris* L. beide Zentralharzgänge nicht nur in der oberen Hälfte, sondern sogar in dem oberen Drittel der Nadel zu beobachten (11). Obgleich ich dem Studium der zentralen Harzgänge keine besondere Beachtung schenkte, ergeben meine Befunde jedoch, dass diese Gänge anders beginnen, als Djaparidze und Wassilewskaja es schildern.

Da jede Tatsache, jede Präzisierung und Ergänzung zu den Angaben, die wir in der Literatur vorfinden, ausser einem theoretischen auch praktischen Wert besitzen, insofern sie uns ein Material liefern, das als «konkretes Kriterium bei Abschätzung der auf Harznutzung untersuchten Holzhaue dienen kann» (13), war es zweckmässig spezielle Beobachtungen über den Anfang,

sowie den Verlauf dieser Gänge in der Nadel anzustellen. Zu diesem Zweck wurden Serien von Präparaten aus in verschiedenen Gegenden der Ukraina gesammeltem Herbariummaterial, sowie aus frischem Material (junge Kiefern aus dem Kanewschen Hegewald) hergestellt.

Die Schnitte wurden mittels eines Rasiermessers mit der Hand ausgeführt, in Abständen von 3 mm von der Basis der Nadel angefangen bis zu der Stelle, wo der Gang kleiner wurde und vermutlich bald endigte. Von dieser Stelle an führte man eine ununterbrochene Schnittserie aus; jeder Schnitt wurde der Reihe nach durchgesehen bis zum völligen Verschwinden des Ganges. Auf Grund dieser Untersuchung kann man folgende Schlüsse ziehen:

1) Die zentralen Harzgänge in der Nadel der *Pinus silvestris* L. nehmen ihren Anfang stets vollkommen ausgebildet in dem Xylem unter dem Parenchymstrahl, zuweilen näher zum Phloem, manchmal neben dem Transfusionsgewebe.

2) In der Nadel abwärts verlaufend, übertreten diese Gänge die Grenze des Xylems und gelangen durch das Transfusionsgewebe bis zur Basis der Nadel, woselbst sie wieder in das Xylem dringen und zwar von der dem Phloem gegenüberliegenden Seite, um dann völlig ausgebildet sich weiter im Zweige auszubreiten.

3) Einige Gänge endigen an der Basis der Nadel ganz so, wie sie anfingen, mit dem Parenchymstrahl.

4) Bei gut belichteten, kräftigen zweijährigen Nadeln alter Bäume der *Pinus silvestris* L. aus Sossnowka, Pirnowo, aus der Umgegend von Kiew, bei der Kreidekiefer aus Artemjewsk, sowie bei einjährigen bis zweijährigen Nadeln junger Kiefern aus Kanew, kann man oft beobachten, dass diese Gänge in der oberen Hälfte, ja sogar im oberen Drittel der Nadel beginnen und dass in jeder Nadel 1—2 Gänge vorhanden sind.

5) Bei 3-jährigen Nadeln junger Kiefern aus Kanew trifft man solche, die 3—4 zentrale Harzgänge aufweisen, aber nicht mehr als vier Harzgänge auf ein Paar Nadeln (bei 12—16 peripheren).

6) An verkümmerten Nadeln alter Waldkiefern beobachten wir weniger Zentralgänge (1 Harzgang auf die Nadel oder sogar auf ein Nadelpaar), und sie beginnen nur in der unteren Hälfte, zuweilen unweit vom Ansatz der Nadel. Bei stark verkümmerten Nadeln an Zweigen unterer Lage sind überhaupt keine Zentralgänge zu finden (den früheren Angaben entsprechend).

7) Die Widersprüche in der Literatur in bezug auf Anzahl und Verlauf der Zentralgänge in der Nadel der *Pinus silvestris* L. lassen sich dadurch erklären, dass die Forscher verschiedenes Material (hinsichtlich der Beleuchtung, Lage der Nadel am Baum, usw.) zu ihren Untersuchungen verwandten.

8) Es ist durchaus notwendig bei anatomischen Untersuchungen der Nadelstruktur solche Faktoren, wie Alter des Baumes, Beleuchtung, Lage der Nadel am Baum usw., in Betracht zu ziehen.

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*PHYSIOLOGY*

# ON THE QUESTION OF LABILITY OF CONDITIONED REFLEXES IN TWINS

By I. KANAEV

*(Communicated by L. A. Orbeli, Member of the Academy, 24. XII. 1940)*

According to data previously published by the author, one-egg human twins (OET) seem to develop conditioned reflexes, as a rule, simultaneously. Thus, for instance, the twins Sm. (ten-year-old boys) developed their first conditioned reflex (in response to the metronome with a frequency of 200 strokes) on the third day of the experiment, another pair (girls L. thirteen years of age) formed a conditioned reflex to the same stimulus on the 6th day, and so on. One pair of OE twins (girls K. of 7 years) developed a conditioned reflex with a difference of one day, which could be accounted for by the unfavourable effect the day in question has had on the girl who lagged behind.

The two-egg twins (TET)—only 3 pairs have come under the author's observation—have always shown a marked discrepancy as to the day on which the conditioned reflex is to appear. Of the above-mentioned 3 pairs the 10-year-old girls Lor. developed a conditioned reflex with a difference of two days, i. e. one on the second day of the experiment, the other one on the fourth. The same occurred with the second pair (11-year-old girls M.): the conditioned reflex appears in one of them on the 13th, and in the other one as late as the 15th day. In the 3rd pair (of different sex) the boy 11 years of age lagged 7 days behind the girl, who developed the conditioned reflex on the 3rd day.

It may be seen that the time it takes to develop a conditioned reflex in children of about the same age differs markedly, and that the days of its appearance within the pair of TET never coincided.

In connexion with these data it was of interest to make a more detailed study of the lability of the conditioned reflex in twins. Some material on this question was obtained by the author as a result of a prolonged experiment (which lasted about a year, from February 1939 up to and including February 1940) with one pair of twins (OE) Lora and Lucy K. born on the 20th of August 1925. The experiment was carried out after Krasnogorsky's method with both gl. parotis. A conditioned reflex came to show rather distinctly on the 4th day of the experiment and was very small within the first days; and afterwards the size of the conditioned reflex remained quite negligible, mostly 2—6 drops. Little difference was seen in the response to the strength of the stimulus.

These children have been subjected to the following stereotype treatment:

1. Metronome with a frequency of 200 strokes (M 200) reinforced (+).
2. Bell, ditto.
3. Red lamp, ditto.
4. Metronome with a frequency of 100 strokes (M 100) not reinforced (—).
5. Metronome 200 reinforced (+).

This stereotype procedure was applied in the following order: beginning from the 60th combination, reinforced by the metronome 200, in response to

which the first conditioned reflex had been elaborated, differentiation was introduced to the metronome with a frequency of 100 strokes (M 100) not reinforced.

The first time under the action of the M 100 both girls were getting ready to obtain reinforcement and gave the usual conditioned secretion. The second time none of them was prepared, one yielded 1 drop of conditioned secretion, the other one 2 drops. Upon the 5th application, no secretion whatever followed; upon the 6th and 7th—1—2 drops at a time; the 8th application failed to produce secretion; and such was the state of affairs with very few exceptions, throughout the experiment. It can be evidently deduced that they have developed simultaneously the inhibitory reflex. After an interval during the summer the first application of M 100 produced in one of the girls 2 drops, in the other one 1 drop, while the second application produced no secretion whatever.

After M 100 the bell was applied, the sound of which somewhat frightened the children. Both of them were ready for it at once and yielded conditioned secretion.

The red lamp was introduced after the bell. The conditioned reflex to it did not appear at once. With the second application both of them started getting ready, but the secretion was negligible: 1—2 drops, and sometimes there was none at all. Only the 6th time each of them yielded 3 drops, and further the conditioned secretion was nearly uninterrupted and consisted of about 2—5 drops. It may be seen, that apart from some small differences, the conditioned reflex in response to the red lamp developed practically simultaneously.

When the stereotype procedure became sufficiently stabilized (on the 9th of January—after the red lamp has been applied the twenty third time), a rearrangement of the stimuli was made, according to the following scheme (the first one) with the number of drops (for 30 sec.) to each stimulus indicated below:

| | M 200 (+) | M 200 (+) | M 100 (—) | Red lamp (+) | Bell (+) |
|---|---|---|---|---|---|
| Lora . . . . . | 2 | 2 | 2 | 6 | 3 |
| Lucy . . . . . | 4 | 4 | 0 (did not get ready) | 4 | 5 |

A few days later the stimuli were applied in a different order.

| | M 200 (+) | M 100 (—) | Red lamp | Bell | M 200 |
|---|---|---|---|---|---|
| Lora . . . . . | 6 | 3 | 4 | 1 | 2 |
| Lucy . . . . . | 6 | 0 | 4 | 7 | 5 |

On the day after to-morrow the usual stereotype procedure was applied, with the following result:

| | M 200 (+) | Bell | Red lamp | M 100 (—) | M 200 |
|---|---|---|---|---|---|
| Lora . . . . . | 2 | 2 | 2 | 0 | 0 |
| Lucy . . . . . | 8 | 3 | 3 | 1 (did not get ready) | 3 |

Two days later was repeated the rearrangement of the first type and the following results were obtained:

| | M 200 (+) | M 200 (+) | M 100 (—) | Red lamp (+) | Bell (+) |
|---|---|---|---|---|---|
| Lora . . . . . | 4 | 5 | 0 | 3 | 2 |
| Lucy . . . . . | 4 | 5 | 0 | 3 | 3 |

During the first 2 experiments with the rearrangement Lora produced secretion in response to M 100 (—) twice, whereas Lucy yielded none at all. In the last experiment the two girls exhibited great similarity.

Then I passed to experiments with modification, little time being left at my disposal (the parent urged me to finish my work with the children, so as to enable them to put more work at school during the third quarter, their marks having been far from excellent).

On the 22nd of January 1940 was performed the first experiment with modifications consisting in that M 100 in the stereotype procedure was reinforced and M 200 following thereafter was not. The metronome of the same rhythm applied in the first place of the stereotype procedure remained reinforced, which made the work with M 200 somewhat more complicated.

The next day, already with the second application Lora guessed the change and formulated clearly the meaning of it, whereas Lucy seemed not to be aware of it, although both of them failed to produce secretion to M 100. The third time (on January 24) the two of them got ready to seize the reinforcement from the tray at the sound of M 100, but not at once. Secretion: in Lucy —none, in Lora—1 drop. The 4th time Lora did not get ready immediately, whereas Lucy got ready at once and both gave conditioned secretion 2 drops each. After that the two of them were getting ready at once and yielded on the fifth application 1 drop each, and subsequently still more: 2—4 drops each.

With M 200 becoming negative when shifted to the last place of the stereotype, the transformation proceeded at a slower rate. The third time Lucy was not getting ready any more, whereas Lora was. Only the 9th time they both failed to produce secretion to M 200 at the end of the stereotype procedure, whereas they gave 3 drops each when the same was applied at the beginning. No secretion was forthcoming when M 200 (—) was applied the tenth time, on February 6, 1940, when the author had to discontinue temporarily the investigation of these twins.

They manifested very great similarity when M 100 was changed from the negative to the positive and somewhat less when M 200 was changed from the positive to the negative, perhaps, on account of the task being more complicated, since M 200 applied at the beginning of the stereotype procedure remained reinforced.

It would be of interest to continue observation on this pair, as well as to investigate the stereotype procedure in other pairs of OET and TET to make clear, whether the similarity between the OET is actually much greater than between the TET as regards the elaboration of conditioned reflexes, as well as their lability.

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*ZOOLOGIE*

# ÜBER DIE ERNÄHRUNG VON *TYROGLYPHUS FARINAE* L. UND *TYROPHAGUS NOXIUS* ZACHV. IN DEN SAMEN VON KOK-SAGHYZ

Von M. S. GHILAROV

*(Vorgelegt von I. I. Schmalhausen, Mitglied der Akademie, den 25.IX.1940)*

Die phytopathologische Expertiese des Samenmaterials von Kok-saghyz zeigt, dass die Oberfläche der Samen gewöhnlich stark von verschiedenen Pilzen befallen ist. Bei erhöhter Feuchtigkeit verkleben sich zuerst die Samen von Kok-saghyz und werden nach einigen Tagen dicht mit Myzelium bedeckt.

Die verbreitesten Vertreter der Mykoflora der Samen von Kok-saghyz stellen die Arten der Gattungen *Epicoccum*, *Fusarium*, *Cladosporium*, *Alternaria*, *Torula*, *Brachysporium*, *Aspergillus*, *Penicillium* u. a. dar (1). Bei Durchführung der Versuche zur Aufklärung der Schädlichkeit von *Tyroglyphus farinae* L. und *Tyrophagus noxius* Zachv., die nicht selten in den Samen von Kok-saghyz vorgefunden werden, hat man beobachtet, dass *T. farinae* und *T. noxius* die Entwicklung von Pilzen auf den Samen dieser kautschukbildenden Pflanze hemmen*.

Die Versuche wurden in entomologischen Reagenzgläschen von 5—7 $cm^3$ Fassung ausgeführt. Die Samen wurden auf den Boden der Reagenzgläschen gelegt und letztere mit befeuchteten Wattenstöpseln verschlossen. Dadurch entstand in den Reagenzgläschen eine mit Wasserdampf gesättigte Atmosphäre, jedoch ohne kontakte Befeuchtung der Samen. In jedes Reagenzgläschen wurden 100 gut ausgefüllte Samen von Kok-saghyz abgezählt.

Im ersten Versuch wurden die Samen in vier Reagenzgläschen ohne Milben gelassen, in vier Reagenzgläschen waren je 100 Exemplare von *T. farinae*, in vier—je 100 Exemplare von *T. noxius* eingeführt. Als Kontrolle brauchte man je 100 Samen in vier mit trockenen Wattenstöpseln abgeschlossene Reagenzgläschen. Der Versuch wurde bei Zimmertemperatur (ungefähr bei 18°) ausgeführt. Der Zustand der Samen in den Reagenzgläschen wurde periodisch nachgeprüft, und nach Beendigung des Versuches die Keimfähigkeit und Keimenergie der Samen bestimmt. Die Versuchsergebnisse sind in Tabelle 1 angegeben. Der Versuch wurde mit Samen desselben Musters in 10-facher Wiederholung (Tab. 2) ausgeführt.

Aus den in den Tabellen 1 und 2 angeführten Zahlen ist ersichtlich, dass sich in Gegenwart von *T. farinae* und *T. noxius* auf den Samen von Kok-saghyz kein Schimmel bildet. Eine 20 Tage lang andauernde Einwirkung der Milben auf die Samen von Kok-saghyz übte keinen Einfluss auf die Keimfähigkeit der letzteren aus. Unter gleichen Bedingungen (in feuchter Atmosphäre) war die Keimfähigkeit der Samen mit Milben sogar höher als bei Samen ohne Milben, die der Einwirkung von Pilzen ausgesetzt waren.

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* Die Arbeit wurde unter Mitwirkung der Mitarbeiterin des Laboratoriums V. Z. Melnikowa ausgeführt.

Tabelle 1

Einfluss der Milben auf den Zustand der Samen von Kok-saghyz (Der Versuch wurde am 4.III.1940 angestellt, am 25.III abgeschlossen)

| Versuchsvariante | Zustand der Samen | | Keimfähigkeit der Samen in % | Keimenergie in % |
|---|---|---|---|---|
| | 14.III | 25.III | | |
| Ohne Milben (in feuchter Atmosphäre) | In allen Reagenzgläschen verklebt und mit Myzelium bedeckt | In allen Reagenzgläschen dicht mit Myzelium bedeckt | 55.5±9.47 | 53.25 |
| Mit Milben *T. farinae* (in feuchter Atmosphäre) | Normal (die Samen verstreuen sich) | Normal (die Samen verstreuen sich) | 67.0±4.96 | 64.75 |
| Mit Milben *T. noxius* (in feuchter Atmosphäre) | Ditto | Ditto | 67.0±6.08 | 65.75 |
| Kontrolle (trockene Samen) | » | » | 74.5±1.55 | 69.25 |

Tabelle 2

Einfluss der Milben auf den Zustand der Samen von Kok-saghyz (Der Versuch wurde am 25.III.1940 angestellt, am 15.IV abgeschlossen) (Kontrolle gemeinsam mit dem ersten Versuch)

| Versuchsvariante | Zustand der Samen | | | | Keimfähigkeit der Samen in % | Keimenergie in % |
|---|---|---|---|---|---|---|
| | 2.IV | 4.IV | 7.IV | 15.IV | | |
| Ohne Milben (in feuchter Atmosphäre) | Die Samen waren verklebt | Die Samen waren verklebt | Die Samen dicht mit Myzelium bedeckt | Die Samen dicht mit Myzelium bedeckt | 66.12±1.87 | 66.1 |
| Mit Milben *T. farinae* (in feuchter Atmosphäre) | Normal | Normal | Normal | Normal | 72.78±1.97 | 69.33 |
| Mit Milben *T. noxius* (in feuchter Atmosphäre) | » | In 9 Reagenzgläschen normal, in einem Gläschen verklebt | » | » | 71.44±2.34 | 66.67 |

Die geringe Empfindlichkeit der Samen von Kok-saghyz gegenüber der Einwirkung der *T. farinae* und *T. noxius* (sowie auch der Schimmelpilze) erklärt sich dadurch, dass der Embryo von Kok-saghyz durch 3 widerstandsfähige Hüllen geschützt ist. Die äussere Fruchthülle besteht aus einer Schicht verholzter und einiger Schichten verkorkter Zellen. Dann folgt die Samenhaut (die aus dem Integument der Samenanlage gebildet wird). Die innere Hülle bildet eine doppelte Schicht elastischer, dichter, dickwandiger Zellen (Reste des Endosperms) (²). Die intakte Fruchthülle stellt ein fast unüberwindliches Hindernis für die Milben dar; das Myzelium der Pilze bildet sich anfangs ebenfalls nur auf der Fruchthülle. Die Hemmung des Wachstums des Myzeliums auf den Samen von Kok-saghyz in Gegenwart von Milben erklärt sich dadurch, dass diese Milben sich von den auf der Oberfläche der Samen entwickelnden Pilzen ernähren.

Dass die Milben das Myzelium in den Samen von Kok-saghyz wirklich vernichten, davon konnten uns die Versuche der Besiedelung der mit Myze-

lium bedeckten Samen von Kok-saghyz durch *T. farinae* und *T. noxius* überzeugen. Den 4—5 Mai 1940 wurden in 4 Reagenzgläschen mit verklebten Samen je 200 *T. farinae*, in 4 Reagenzgläschen je 200 *T. noxius* gebracht, 4 Gläschen blieben zur Kontrolle. Alle Reagenzgläschen waren mit feuchten Wattenstöpseln verschlossen. Bei Prüfung nach 3—4 Tagen (8.V) stellte sich heraus, dass in allen Reagenzgläschen mit Milben die Samen von Myzelium frei waren und sich leicht verstreuten, während in den Reagenzgläschen ohne Milben die Samen zu Klümpchen verklebt blieben und sich mit einem dichten Filz von Myzelium bedeckten.

Am 9. V. 1940 wurde ein ebensolcher Versuch mit Samen, die stark mit Myzelium von Schimmelpilzen bedeckt waren, angestellt (*T. farinae* und *T. noxius* wurden in grosser Menge ohne genauere Zählung verwendet). Die Prüfung nach 6 Tagen (15. V) zeigte, dass in den Reagenzgläschen mit Milben (mit Ausnahme von einem Reagenzgläschen mit *T. farinae*) das Myzelium verschwunden war, und die Samen sich leicht verstreuten, während in der Variante ohne Milben die Samen zu kompakten Klümpchen verklebt blieben, die an den Wänden der Reagenzgläschen hafteten und mit einem Filz von Myzelium bedeckt waren.

Bemerkenswert ist das Verhalten von Milben, die in unverschimmelte und verklebte Samen von Kok-saghyz gebracht wurden. Bei Verbringung der Milben in Reagenzgläschen mit verschimmelten oder verklebten Samen, kriechen die Milben gleich zwischen die Samen, während die Milben in den Reagenzgläschen mit reinen Samen nicht nur unter den Samen, sondern auch an den Wänden der Reagenzgläschen umherkriechen.

Alle angeführten Angaben stellen fest, dass *T. farinae* und *T. noxius* sich in den Samen von Kok-saghyz auf Kosten des Myzeliums verschiedener Pilze, die sich auf den Fruchthüllen entwickeln, ernähren.

Die Fähigkeit zur Myzetophagie trägt zur Erklärung des Vorkommens von *T. farinae* und *T. noxius* in verschiedenen Samen, die durch widerstandsfähige, für sie unzugängliche Hüllen geschützt sind, bei. Diese Myzetophagie erklärt auch im wesentlichen, weshalb *T. farinae* und *T. noxius* bei genügender Feuchtigkeit in den verschiedensten Substraten gefunden werden können. Die Versuche beweisen jedoch nicht, dass die Milben für die Samen von Kok-saghyz unschädlich sind. Bei länger dauernden Versuchen wurde beobachtet, dass bei sehr ungünstigen Bedingungen der Aufbewahrung (Feuchtigkeit der Samen von 15—16% bei einer konstanten Temperatur von 20°) die Keimfähigkeit der nicht mit *T. farinae* und *T. noxius* besiedelten Samen nach 70 Tagen bis zu 30.2% und bei den mit Milben besiedelten bis zu 20.6—24.4% abnahm. Es ist möglich, dass die der langandauernden Einwirkung der Pilze ausgesetzte Fruchthaut auch der Zerstörung durch die Milben zugänglich wird.

Die Vernichtung von *T. farinae* und *T. noxius* in den Samen von Kok-saghyz durch Trocknen der befallenen Samen und darauffolgender Naphtalinisierung (3) ist leicht erreichbar. Die Samen von Kok-saghyz lassen ebenfalls eine Fumigation durch Schwefelkohlenstoff, Chlorpikrin (4) und Dichloraethan in für *T. farinae* und *T. noxius* letalen Dosen, zu.

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*ZOOLOGIE*

# ÜBER DIE SCHLUNDZÄHNE BEI GATTUNGSBASTARDEN VON KARPFENFISCHEN

Von N. I. NIKOLJUKIN

*(Vorgelegt von I. I. Schmalhausen, Mitglied der Akademie, den 18. XII. 1940)*

Die Untersuchung der Schlundzähne bei Gattungsbastarden der *Cyprinidae* ist nicht nur von grossem Interesse für die Systematik der Bastarde selbst, sondern auch für die Erforschung der Evolution der Schlundzähne in dieser Familie der Fische(3). Ausser den Schlundzähnen wurden auch andere systematische Merkmale bei kleinen Fischen (Länge von 2.5 bis 18 cm) der Gattungsbastarden von *Cyprinidae* im Alter von einigen Monaten bis 6 Jahren untersucht. Die Bastarden wurden durch künstliche Befruchtung des Laichs erhalten. Die Fische, welche bei den Kreuzungen verwendet wurden, erhielten wir aus den Seen und Flüssen des oberen Don.

Kurze Angaben über die Schlundzähne einiger Gattungsbastarde von *Cyprinidae* finden sich in meiner vorläufigen Mitteilung (4). Bei der Darlegung der erhaltenen Resultate beginnen wir mit solchen Gattungsbastarden, welche wir durch die Kreuzung solcher Arten von Karpfenfischen erhielten, die durch eine einreihige Schlundzähneformel gekennzeichnet sind.

*Carassius carassius* L. ♀ × *Tinca tinca* L. ♂. Über die Schlundzähne der Hybriden zwischen Karausche und der Schleie sind in der Literatur keine Angaben vorhanden, so dass in bezug auf dieses Merkmal die Bastarden zum ersten Mal untersucht wurden. Bei 78 Bastarden konnten wir im Alter ungefähr von 1 Jahr ohne Ausnahme immer nur eine einreihige Schlundzähneformel 4—4 feststellen, welche für die Karausche charakteristisch ist, bei der Schleie (5) aber selten angetroffen wird. Somit sehen wir, dass diese beiden Arten eine gemeine Zahnformel haben. Die Schlundzähne der Bastarden stehen der Form nach denen der Karausche etwas näher, obgleich auch an einigen Zähnen die Spitzen die Form eines Häckchens haben, was für die Zähne der Schleie und für die Karausche nicht charakteristisch ist.

*Rutilus rutilus* L. ♀ × *Tinca tinca* L. ♂. Bastarden zwischen der Plötze und der Schleie sind bis jetzt noch nicht beschrieben. Von 24 Hybriden konnten wir bei 23 die gleiche Formel 5—5, und nur bei einem 1.5—5 auftreffen. Somit sehen wir, dass bei den Bastarden die Formel der Schlundzähne viel weniger variiert als bei den Ausgangsarten. Berg (6) führt für die Plötze 6—5, selten 5—5 oder 6—6 Schlundzähne an, für die Schleie 4—5, 5—4, 5—5 und 4—4. Von diesen Zahnformeln wird nur 5—5 bei beiden Arten angetroffen, welche auch für die Hybriden charakteristisch ist. Der Form nach sind die Zähne der Bastarden in den meisten Fällen intermediär.

*Rutilus rutilus* L. ♀ × *Chondrostoma nasus* L. (beide reziproke Formen). Bastarde sind in der Literatur nicht beschrieben. Bei 23 Hybriden Plötze ♀ × Schwarzbauch ♂ konnten wir folgende Schlundzähneformeln feststellen: 6—5 (bei 14 Individuen) und 6—6 (bei 9), und von 15 Hybriden Schwarz-

bauch ♀ × Plötze ♂ 6—5 (bei 8 Individuen), 6—6 (bei 4) und 5—5 (bei 3). Bezrukowa (7) konnte bei 200 Exemplaren des *Chondrostoma nasus* aus dem Fluss Don folgende Schlundzähneformeln feststellen: 6—5, 6—6, 5—5, 5—6 und 7—6. Nur die ersten drei dieser Formeln treffen nicht nur bei dem Schwarzbauch, sondern auch bei der Plötze und nur auch diese konnten wir bei den Hybriden feststellen, wobei auch hier sowie bei den Ausgangsarten die Zahnformel 6—5 vorherrscht. Was die Form der Schlundzähne bei den Bastarden anbelangt, so unterscheiden sie sich in den meisten Fällen von den Zähnen der Plötze durch eine verlängerte und mehr gedrängte Krone, was sie in gewissem Grad den messerartigen Zähnen des Schwarzbauches nähert, haben aber zum Unterschied von letzteren an den Spitzen Häckchen. Wir konnten aber auch bei einigen Bastarden auch die für den Schwarzbauch typische messerartige Zähne feststellen.

*Rutilus rutilus* L. × *Abramis brama* L. (beide reziproke Formen). Bei 111 Hybriden von Plötze ♀ × Brachse ♂ konnten wir folgende Schlundzähneformeln feststellen *: 6—5 (83), 5—5 (10), 5—6 (8), 1.6—5 (4), 6—5.1 (2), 6—6 (2), 1.6—6.1 (1), 6—4 (1); und bei 62 Hybriden Brachse ♀ × Plötze ♂: 6—5 (50), 5—5 (8), 5—6 (3), 1.6—5 (1). Hieraus sehen wir, dass auch in diesem Fall die Zahnformeln vorherrschen, welche die beiden gekreuzten Arten gemein haben—6—5 und 5—5 (besonders die erste Formel). Berg (6) führt auch nur diese Zahnformel für diesen Bastard an. Die Zähne der Bastarden haben meistens an den Spitzen Häckchen und auf der Kaufläche Rinnen; einige von ihnen sind gezackt (manchmal faltig), was sie von den glatten Zähnen der Brachse unterscheidet und den faltigen Zähnen der Plötze nähert.

Die zweite Gruppe bilden die Bastarden, welche wir bei der Kreuzung der Karpfenfische erhielten, von denen sich die eine Art durch einreihige und die andere durch zweireihige Schlundzähne auszeichnet.

*Rutilus rutilus* L. ♀ × *Leuciscus danilewskii* (Kessler) ♂. Die Schlundzähne dieses Hybrids (hier das erste Mal beschrieben) zeigen eine grosse Variation der Zahl und Anordnung nach. Bei 78 Exemplaren wurden folgende Zahnformeln festgestellt: 1.6—5.1 (19), 2.6—5.1 (13), 1.5—5.1 (9), 1.6—5.2 (9), 2.6—5.2 (7), 6—5.1 (4), 2.5—5.2 (2), 1.5—5.2 (2), 2.5—5.1 (2), 1.5—5 (2), 5—5.2 (2), 2.5—5 (1), 2.6—6.1 (1), 2.5—6.1 (1), 6—5.2 (1), 1.6—6 (1), 6—5 (1), 5—5 (1). Hieraus sehen wir, dass bei der grössten Anzahl der untersuchten Bastarde (bei 65 von 78) zweireihige Zähne an beiden Seiten vorhanden sind; bei wenigen von ihnen (bei 11 von 78) sind die Zähne auf einer Seite einreihig, auf der anderen zweireihig und nur bei zwei Individuen haben wir einreihige auf beiden Seiten; in diesen letzten Fällen finden wir bei den Hybriden eine Zahnformel, von 6—5 und 5—5, welche für die Plötze charakteristisch ist. Bei den meisten Bastarden ist die Zahl der äusseren (kleinen) Zähne geringer als dieselbe bei der zweireihigen Zahnformel des *Leuciscus danilewskii* (2.5—5.2), welche nur bei zwei Individuen gefunden wurde. Im allgemeinen kann gesagt werden, dass die Hybriden nach der Zahnformel eine Reihe allmählicher Übergänge von *Leuciscus danilewskii* zu *Rutilus rutilus* darstellen. An den Zähnen der Bastarden sind Häckchen und Falten (oder kleine Zäckchen) vorhanden.

*Rutilus rutilus* L. ♀ × *Blicca bjoerkna* L. ♂. Bei 47 Bastardindividuen wurden folgende Formeln der Schlundzähne gefunden: 1.5—5.1 (12), 1.6—5.1 (9), 1.6—5.2 (5), 2.6—5.1 (4), 1.5—5 (3), 5—5.1 (2), 1.5—6.1 (2), 1.5—6.2 (2), 6—5.1 (2), 5—5 (2), 2.6—5.2 (1), 1.6—5 (1), 1.5—5.2 (1), 2.5—5.1 (1). Was über die Zahl und die Anordnung der Schlundzähne der Hybriden von *Rutilus* × *Leuciscus* gesagt wurde, bezieht sich auch in gewissem Grad auf

* Die Zahl der Individuen dieses oder jenes Hybrids mit dieser oder anderer Zahnformel wird durch die in Klammern eingeschlossene Zahl (nach der Formel) angegeben.

die Hybriden von *Rutilus* × *Blicca*. Dies ist auch verständlich, da ja für die Wimbe dieselbe Zahnformel (2.5—5.2) wie für *Leuciscus* charakteristisch ist. Nur in zwei Fällen konnten wir die einreihige Formel 5—5 und niemals 6—5 feststellen. Wahrscheinlich kommt auch die letztgenannte Formel bei diesem Hybride vor, nur sehr selten; aber es ist auch möglich, dass in einigen Fällen, wo darüber berichtet wird, dass als Bastard zwischen der Plötze und der Wimbe die Hybriden zwischen der Plötze und der Brachse angenommen wird, bei welchen diese Formel bedeutend öfter als andere vorkommt. Die Zähne der Hybriden Plötze × Wimbe besitzen auf der Kaufläche Rinnen und an den Spitzen Häckchen; von denen einige leicht gezackt sind.

*Abramis brama* L. × *Blicca bjoerkna* L. (beide reziproke Formen). Bei 23 Bastarden Brachse ♀ × Wimbe ♂ wurden folgende Formeln der Schlundzähne festgestellt: 1.5—5.1 (8), 1.5—5 (4), 5—5.1 (3), 2.5—5.1 (3), 2.5—5.2 (2), 1.5—5.2 (1), 2.6—5.2 (1), 1.6—6.2 (1); und bei 44 Bastarden Wimbe ♀ × Brachse ♂: 1.5—5.1 (17), 1.5—5 (6), 5—5.1 (6), 1.5—5.2 (5), 5—5 (2), 5—5.2 (2), 2.5—5.2 (2), 2.5—5 (1), 2.5—5.1 (1), 1.5—4.2 (1), 1.5—4 (1). Somit sehen wir, dass bei beiden reziproken Hybriden eine zweireihige Zähneanordnung vorherrscht, wobei die Formel 1.5—5.1 am häufigsten vorkommt; die Gesamtzahl der Zähne dieser Formeln stellt die mittlere Zähnezahl dar, welche die Brachse (5—5) und die Wimbe (2.5—5.2) charakterisieren. Diese Formeln der Ausgangsarten kommen, wenn auch selten, auch bei den Hybriden vor. Die Zähne der Hybriden haben an den Spitzen stark gebogene Häckchen, auf der Kaufläche sind sie schräg geschnitten; einige sind gezackt, was sie von den glatten Zähnen der Ausgangsarten unterscheidet.

*Abramis brama* L. × *Scardinius erythrophtalmus* L. (beide reziproke Formen). Bei 40 Exemplaren der Bastarden von Brachse ♀ × Rotauge ♂ konnten folgende Formeln der Schlundzähne festgestellt werden: 1.5—5.1 (8), 2.5—5.2 (8), 2.5—5.1 (7), 1.5—5.2 (6), 2.6—5.1 (3), 5—5.1 (2), 3.5—5.2 (1), 2.6—5.2 (1), 2.5—4.1 (1), 2.5—5 (1), 1.5—5 (1), 5—5 (1); und bei 39 Hybriden von Rotauge ♀ × Brachse ♂: 1.5—5.1 (11), 1.5—5.2 (7), 2.5—5.2 (5), 2.5—5.1 (4), 2.5—5 (2), 5—5.1 (2), 5—5 (2), 5—5.2 (1), 1.5—5 (1), 2.5—5.3 (1), 1.5—6.1 (1), 1.6—5 (1), 2.5—4 (1). Die angeführten Angaben zeigen, dass bei den Hybriden die zweireihigen Formeln der Schlundzähne vorherrschen, und zwar: 1.5—5.1, 2.5—5.2, 1.5—5.2 und 2.5—5.1. Diese Formeln sind intermediär hinsichtlich der Formel, welche für Brachse (5—5) charakteristisch ist (bei drei Hybriden festgestellt) und der Formel des Rotauges (3.5—5.3) (unter den Hybriden nicht gefunden); der letzten Formel stehen die Formeln 3.5—5.2 und 2.5—5.3 nahe, welche an einzelnen Hybriden gefunden wurden. An den Zähnen sind klar Häckchen und Zacken zu sehen.

Die dritte Gruppe von Bastarden erhielten wir durch die Kreuzung solcher Arten der *Cyprinidae*, wo jede Art eine zweireihige Formel von Schlundzähnen besass.

*Scardinius erythrophtalmus* L. × *Blicca bjoerkna* L. (beide reziproke Formen). Bei 55 Bastarden von Rotauge ♀ × Wimbe ♂ zeigte die Formel der Schlundzähne folgende Variationen: 2.5—5.2 (21), 3.5—5.3 (15), 2.5—5.3 (7), 3.5—5.2 (6), 1.5—5.2 (1), 2.5—5.1 (1), 1.5—5.1 (1), 2.6—5.2 (1), 2.6—6.2 (1), 2.4—6.2 (1); und bei 45 Bastarden von Wimbe ♀ × Rotauge ♂: 2.5—5.2 (16), 3.5—5.3 (9), 2.5—5.3 (7), 3.5—5.2 (5), 1.5—5.2 (3), 2.5—5.1 (1), 3.5—5.1 (1), 2.6—5.2 (1), 2.6—5.1 (1), 2.4—5.2 (1). Hieraus ist zu sehen, dass bei 100 untersuchten Bastarden die Schlundzähne ausschliesslich zweireihig waren. Am häufigsten konnte die Formel festgestellt werden, welche beide Ausgangsarten gemein haben, und zwar 2.5—5.2 (37%), welche für die Wimbe charakteristisch ist, aber als Ausnahme auch bei dem Rotauge angetroffen wird, und die Zahnformel 3.5—5.3 (24%), welche dem Rotauge charakterisiert, aber auch selten bei der Wimbe vorkommt.

Von den anderen Zahnformeln konnten bei den Hybriden die Formeln 2.5—5.3 (14%) und 3.5—5.2 (11%) am häufigsten festgestellt werden, welche intermediär und für die Ausgangsarten typisch sind. Die Zähne haben klar ausgeprägte Häckchen und Zacken; nach diesen Merkmalen stehen sie den Zähnen des Rotauges näher als denen der Wimbe.

*Alburnus alburnus* L. ♀ × *Scardinius erythrophtalmus* L. ♂. In diesem Fall wurden die Schlundzähne an 48 Bastarden untersucht. Bei 29 Individuen wurde die für die Schneiderfische typische Zahnformel 2.5—5.2 festgestellt, welche (zwar sehr selten) auch bei dem Rotauge vorkommt, und somit gemein für beide Ausgangsarten ist. Bedeutend seltener wird an den Hybriden die intermediäre Formel der Ausgangsarten 3.5—5.2 (bei 8 Individuen) und 2.5—5.3 (bei 7) angetroffen, und noch weniger war die für das Rotauge charakteristische Formel 3.5—5.3 (bei 2) vertreten. Ausser den genannten Formeln, wurde bei einem Bastard 2.5—5.1 und bei einem anderen 4.5—5.2 gefunden. An den Zähnen sind Häckchen und Zacken vorhanden, welche aber bei den Hybriden stärker als bei den Schneiderfischen und geringer als bei den Rotaugen zum Ausdruck kommen.

Besondere Beachtung verdienen die von uns durch die Kreuzung des *Carassius carassius* L. (einreihige Zähne) und *Cyprinus carpio* L. (dreireihige Zähne) gezüchteten Hybriden, beide reziproke Formen. Bei solchen Bastarden ist eine zweireihige Formel der Schlundzähne vorherrschend (1.4—4.1). Die vorgefundenen Variationen der Zahl und Anordnung der Zähne sind in meinen Arbeiten ([8],[9]), welche diesen Hybriden gewidmet sind, beschrieben. Hier sei nur bemerkt, dass von 100 Hybriden von dem Spiegelkarpfen ♀ × × Karausche ♂, nur bei 5 je 3 Zähne in der inneren Reihe (von einer oder von zwei Seiten) vorhanden waren, in allen anderen Fällen standen je 4 Zähne.

Auf Grund der dargelegten Tatsachen kann man folgende allgemeine Schlussfolgerungen ziehen. 1) Wenn bei zwei gekreuzten Arten der Karpfenfische von den verschiedenen Schlundzähneformeln auch gleiche vorhanden sind, so herrschen bei den Bastarden die letzteren vor. 2) Wenn bei den gekreuzten Arten die eine Art einreihige und die andere zweireihige Zähne besitzt, so sind die Bastarden der Zähnezahl nach in den meisten Fällen intermediär. Jedoch bei solchen Bastarden herrscht eine zweireihige Zahnanordnung vor, was für die Richtigkeit der Anschauung einiger Autoren ([1],[2],[3]) spricht, wonach die Einreihigkeit der Schlundzähne von den Karpfenfischen sekundär erworben wurde. Von diesem Standpunkt aus, sind die seltenen Fälle, wo nach der Kreuzung Fische mit einreihigen Zähnen, Hybriden mit zweireihigen Zähnen erhalten werden, ein Fall von Atavismus. 3) Die Tatsache, dass die Schlundzähne bei einigen Bastarden etwas stärker gezackt und die Häckchen mehr ausgeprägt sind als bei den Ausgangsarten selbst, bestätigt die Anschauung von Vasnezov ([2]), wonach diese Merkmale primitiv sind. 4) Gesetzmässige Unterschiede zwischen den reziproken Formen der Bastarden der Cypriniden bezüglich der Morphologie, Zahl und Anordnung der Schlundzähne konnten nicht festgestellt werden.

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# DIE ENTSTEHUNG DER FAMILIE DER BRACONIDEN IM ZUSAMMENHANG MIT DER EVOLUTION DER UNTERORDNUNG DER SCHLUPF- UND GALLWESPEN *(HYMENOPTERA, HETEROPHAGA)*

Von N. A. TELENGA

*(Vorgelegt von I. I. Schmalhausen, Mitglied der Akademie, den 18. XII. 1940)*

Über die Frage der Entstehung der Familie der Braconiden existieren drei Anschauungen. Nach Handlirsch (3) ist von den parasitären Hautflüglern die Familie der *Ichneumonidae* die älteste, von deren Urform sich einerseits alle übrigen Familien der Schlupf- und Gallwespen, andererseits eine Reihe Familien der Unterordnung der Stechenden (*Aculeata*) absonderten.

Einen völlig entgegengesetzten Standpunkt vertraten Braedly (1) und Brues (2), die annehmen, dass als die älteste der Schlupf- und Gallwespen die Familie der *Evaniidae* (die Familien der *Aulacidae* und *Gasteruptionidae* eingeschlossen) anzusehen ist, denen über die Familie der *Stephanidae* die Familie der *Braconidae* nahesteht. Von der Familie der *Braconidae* sonderte sich die Familie der *Ichneumonidae* ab; diese Verwandtschaft verlief über die Gattung *Lysiognatha* Ash., die in sich die Merkmale, die einigen Vertretern der Familie der *Braconidae* (die Kiefer an den Enden nach aussen gestülpt) und der Familie der *Ichneumonidae* (Äderung der Vorderflügel) zukommen, vereinigte.

Handlirsch legte seiner Hypothese die Ähnlichkeit der Schlupf- und Gallwespen der Familie *Ichneumonidae (Pimplinae)* mit den tertiären Schlupf- und Gallwespen der Familie der *Ephialtitidae* zugrunde, die er für die ersten Schlupf- und Gallwespen hielt, und andererseits, die Tatsache, dass viele Vertreter der Unterfamilie der *Pimplinae* Parasiten der Prachtkäfer und Holzkäfer sind, die die Baumstämme bewohnen, die nach Aussicht genannten Autors die ursprünglichen Wirte der Schlupf- und Gallwespen sind. Braedly legte seiner Hypothese die Anwesenheit des intercostalen Feldes auf dem Vorderflügel bei den *Evaniidae* und der Holzwespen der Familie der *Siricidae* (die bei den *Ichneumonidae* fehlen) zugrunde.

Vor nicht langer Zeit war diese Frage der Gegenstand der Untersuchungen Tillyards (7). Nach Tillyard entstanden die Schlupf- und Gallwespen von einer Abzweigung der Familie der *Oryssidae*. Den *Oryssidae* am nächsten steht die Familie der *Megalyridae*, da diese mit jener der Äderung der Vorderfügel nach ähnlich sind, unterscheiden sich aber durch die Einschnürung zwischen Brust und Hinterleib und das Auftreten der verlängerten Legeröhre. Die Familie der *Evaniidae* (s. lat.) und der *Stephanidae* sind selbständige, ganz alte Zweige, möglicherweise sogar älter als die *Megalyridae*, aber nach anderer Richtung hin spezialisiert. Alle anderen Familien der Schlupf- und Gallwespen entstanden aus den *Megalyridae*. In der Evolution dieser Gruppen bildeten sich zwei Familienkomplexe. In dem einen Komplex bildeten sich Familien, die durch eine vollkommenere Äderung der Vorderflügel charakterisiert sind (*Ichneumonidae*, *Braconidae* u. a.), in dem anderen— Familien mit reduzierter Äderung (*Cynipidae*, *Chalcididae*, *Proctotrupi-*

*dae*); die Familien der letztgenannten Gruppe stehen mit der im Oberen Jura gefundenen Familie der *Heloridae* in Zusammenhang. So gibt Tillyard in der Evolution der Schlupf- und Gallwespen drei Hauptrichtungen an.

Zur Grundlage der angeführten phylogenetischen Konstruktionen der genannten Autoren diente die Äderung der Vorderflügel. Zur Klärung dieser Frage wurde von uns die Äderung der Hinterflügel zugrunde gelegt, was durch folgende Erwägungen bedingt war. Es steht fest, dass bei den Hautflüglern der Hauptarbeitsteil des Flugapparates die Vorderflügel sind; die Hinterflügel dienen nicht dazu, den Körper der Insekten in der Luft zu halten, sondern nur dazu, die Richtung des Fluges zu bestimmen ([5],[6]). Daraus wird wahrscheinlich, dass die Äderung der Vorderflügel relativ schnellen Veränderungen unterliegen muss, während die Äderung der Hinterflügel, die beim Flug der Insekten eine geringe Rolle spielen, sich langsamer verändern muss. Daraus folgt anzunehmen, dass die Äderung der Hinterflügel die altertümlichen Züge der Organisation der Formen wiederspiegeln muss und folglich zuverlässigere Merkmale ergeben kann, die für die Aufstellung der phylogenetischen gegenseitigen Beziehungen zwischen den hauptsächlichen Familien, brauchbar sind. Die Richtigkeit solcheiner Annahme wird dadurch bestätigt, dass, wie bekannt, die Äderung der Hinterflügel in der Ordnung der Schmetterlinge, die einen ähnlichen Flugmechanismus wie die Hautflügler und eine ähnliche Verbindung von Vorder- und Hinterflügeln aufweisen, sehr wichtige Merkmale, die für Klassifikationszwecke und zur Aufstellung der phylogenetischen Beziehungen zwischen den Hauptgruppen der Ordnung verwandt werden, gibt.

Zugleich mit Berücksichtigung der Änderungen in der Äderung der Hinterflügel, die der Klassifikation der Unterordnung der Schlupf- und Gallwespen zugrunde gelegt wurden, wurde von uns der Versuch unternommen, diese mit den Veränderungen im Bau der Genitalien der Männchen und der hauptsächlichen Larvenformen bei den Vertretern der einzelnen Familien in Einklang zu bringen. Legen wir die Äderung der Hinterflügel zugrunde, so können wir in der Unterordnung der Schlupf- und Gallwespen *(Hymenoptera, Heterophaga)* drei Familiengruppen nennen.

Die erste Gruppe, einschliesslich der Familien der *Ichneumonidae* und *Trigonalidae*, wird durch Queradern zwischen den Radial- und Cubitaladern (Abb. 3, 4) charakterisiert. Die Abstammung dieser Familiengruppe ist von den *Siricoidea* her denkbar. Nimmt man als Ausgangsverhältnis die Äderung der Hinterflügel der Familie der *Siricidae*, so muss man annehmen, dass die weitere Evolution in ihrer Äderung den Weg der Reduktion der Spitzen der basalen und der zweiten rücklaufenden Nerv einschlug (Abb. 1). Aus diesem Schema der Äderung ist es nicht schwer das Schema der Äderung der parasitären Holzwespen der Familie der *Oryssidae* (Abb. 2), im weiteren aber der Schlupfwespen der Familien der *Ichneumonidae* und *Trigonalidae* (Abb. 3, 4) abzuleiten.

Die zweite Familiengruppe bilden die Familien der *Braconidae*, *Aphidiidae*, *Cynipidae*, *Chalcididae*, *Proctotrupidae*. In der Äderung der Hinterflügel dieser Familiengruppe ist das völlige Fehlen der Spuren des Jugum und die Lage der Subcostalader charakteristisch, die oberhalb der Flügelbasis in einer gewissen Entfernung vom Rande verläuft, dann aber, ungefähr in der Flügelmitte, aufsneue zum vorderen Rande zieht (Abb. 7—10).

Die Entstehung der Äderung der Hinterflügel, die dieser Familiengruppe eigen ist, ist folgenderweise denkbar. Nehmen wir als Ausgangsform der Äderung ebenfalls den Typus der Familie der *Siricidae*, so muss man vor allem eine Annäherung der Cubital- und Medialadern (das ist in gewissem Grade bei den *Xyelidae* ausgeprägt), dann aber den Schwund der queren Cubitalader und der zweiten rücklaufenden Ader annehmen. Als Resultat

erhalten wir das Äderungsschema der Hinterflügel, das den ältesten Vertretern der Familie der *Braconidae (Agathiinae)* zukommt.

Bei der Bildung dieses Äderungsschemas vollzog sich eine Verschiebung der Subcostalbasis und ein völliger Schwund des Jugum. Im weiteren unterlag im Prozess der Bildung der einzelnen Familien dieser Gruppe die Äderung einer noch stärkeren Reduktion (Substrat- und Medialader verschmolzen, Basal-, dann auch die Medialadern usw. verschwanden).

So ist die Abstammung dieser zwei Familiengruppen der Schlupf- und Gallwespen von den *Siricoidea* her völlig denkbar. In beiden Fällen läuft

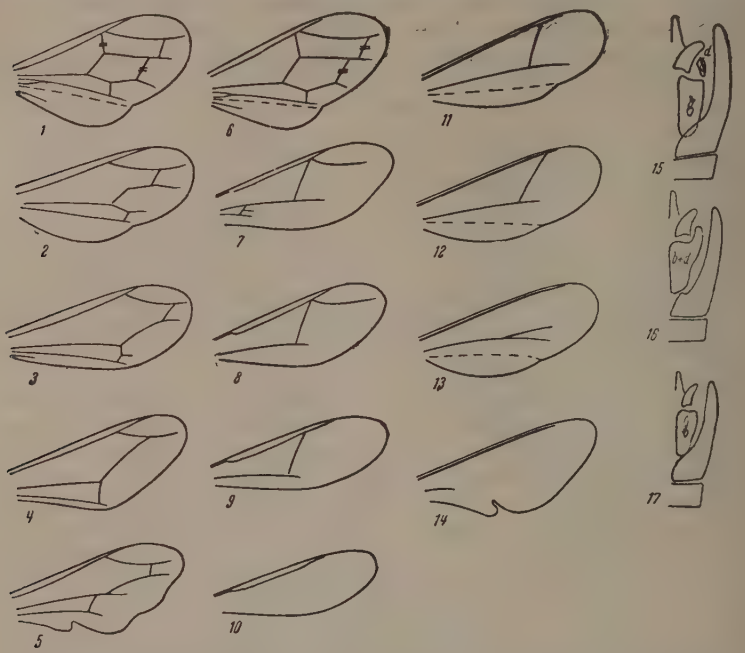

Abb. 1—17. Die Hinterflügel: *1—Siricidae, 2—Oryssidae, 3—Ichneumonidae (Ephialtes), 4—Trigonalidae, 5—Apidae, 6—Siricidae, 7—Braconidae (Agathiinae), 8—Aphidiidae, 9—Cynipidae, 10—Chalcididae, 11—Gasteruptionidae, 12—Aulacidae, 13—Stephanidae, 14—Evaniidae.* Genitalien der Männchen: *15—Ichneumonidae, 16—Braconidae (Halcon), 17—Chalcididae.*

alles auf die Reduktion der Queradern hinaus, mit dem Unterschied, dass in verschiedenen Fällen der Reduktionsprozess von verschiedenen Adern begann.

Die dritte Familiengruppe besteht aus den Familien der *Aulacidae, Evaniidae, Gasteruptionidae, Stephanidae.* In der Äderung der Hinterflügel dieser Gruppe ist die Anwesenheit des Jugum und die Lage der Subcostalader charakteristisch, die in ihrem ganzen Verlauf gerade ist und fast am Flügelrand selbst entlag zieht (Abb. 11—14). Diesen Äderungstyp von der bekannten Familie der Holzwespen abzuleiten ist unmöglich. Vor allem entspricht die Lage der Subcostalader dieser Auffassung nicht.

Die oben angeführten Tatsachen erlauben anzunehmen, dass es in der Unterordnung der *Heterophaga* drei schon seit langem gekennzeichnete phyletische Zweige gibt, die die entsprechenden Familiengruppen ergeben haben. Die gegenseitigen Beziehungen zwischen den einzelnen phyletischen Zweigen in der Unterordnung der Schlupf- und Gallwespen kann man folgender-

weise bestimmen. Der Zweig, zu dem die Familie der *Ichneumonidae* geführt, ist die Hauptgruppe der ganzen Unterordnung und spiegelt seinen Zusammenhang mit der Holzwespe wider. Andererseits, steht unter der Unterordnung der Gall- und Schlupfwespen die Familie der *Ichneumonidae* in den allernächsten Verwandtschaftsverhältnissen mit den *Aculeata* (Abb. 5). Der Zweig, zu dem die Familie der *Braconidae* gehört, nähert sich dem Zweig, der die Familie der *Ichneumonidae* einschliesst, ist aber moderner. Der Zweig, zu dem die *Evaniidae* gehören, ist der älteste und hoch spezialisiert.

Eine gewisse Bestätigung für die Existenz dieser phyletischer Zweige in der Unterordnung der Schlupf- und Gallwespen und der angeführten Beziehungen zwischen ihnen ist der Bau der Genitalien der Männchen. Die Vertreter des älteren Zweiges, zu dem die Familien der *Ichneumonidae*, *Evaniidae* gehören, werden durch eine völlig entwickelte distivolsella charakterisiert, während sie im Zweig, zu dem die Familie der *Braconidae* gehört, fehlt, oder nur in der ältesten Gruppe der Familie der *Braconidae (Agathiinae)* vorhanden ist, dabei bei einigen ein klares Bild ihrer Verschmelzung mit dem basivolcella (Abb. 15—17) ergibt. Die Gemeinsamkeit und Selbständigkeit des Zweiges, zu dem die Familie der *Braconidae* gehört, wird trotz der kolossalen Verschiedenartigkeit der da zugehörigen Formen, durch die Entwicklung der Larven (cyclopoider Habitus) in diesem Zweig bestätigt. Die Bildung dieses Larventypus begann in diesem Zweig in der ältesten Familie der *Braconidae* (*Opiini*) und erwarb seine weitere Entwicklung in den jüngsten Familien (*Cynipidae*, *Chalcididae*, *Proctotrupidae*).

So ist die Stellung der Familie der *Braconidae* im System der Unterordnung der *Heterophaga*, wie sich aus der Analyse der von uns als Grundlage benutzten Merkmale ergibt, verschieden von den Angaben anderer Autoren. Im ganzen steht das von uns gegebene Schema der phylogenetischen gegenseitigen Beziehungen der einzelnen Familien der Schlupf- und Gallwespen den Vorstellungen von Tillyard am nächsten. Wir nehmen allerdings zum Unterschied von der Ansicht des letztgenannten Verfassers an, dass nur die Familien der *Ichneumonidae* und *Trigonalidae* die ancestrale Gruppe der Unterordnung der Schlupf- und Gallwespen ausmachen, während die Familie der *Braconidae* zu einem der Seitenzweige gehört. Andererseits, stellt unserer Ansicht nach der Komplex der Familie der *Chalcididae* (Reduc. Paras. Types, Tillyard) mit der Familie der *Braconidae* einen Zweig dar.

Folgende Angaben über die Zeit der Bildung der einzelnen Familien der Schlupf- und Gallwespen sind vorhanden. Wie die letzten palaeontologischen Untersuchungen zeigten, bewahrheitet sich Handlirschs Auffassung von der Bildung der Familie der Schlupf- und Gallwespen zu Ende des Mesozoikums (Kreide) nicht. Nach Angaben Martynows ([4]) vollzog sich die Bildung der Grundtypen der Äderung der Schlupf- und Gallwespen mindestens zu Beginn des Mesozoikums, zu Beginn der Jurazeit (Lias) aber traf man schon abgesonderte Schlupf- und Gallwespen der Familie der *Evaniidae*. In den Ablagerungen des Jura aus dem Kara-Tau (Kollektion des Palaeontologischen Instituts, gesammelt von Martynow) wurden von uns auch Vertreter der *Braconidae* entdeckt, die zu den gegenwärtigen Tribus der *Hormiini* gehören.

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*EXPERIMENTAL MORPHOLOGY*

# ON THE EFFECT OF CANCEROGENIC SUBSTANCES ON THE HEALING OF SKIN WOUNDS IN MAMMALS

By A. I. SDRUIKOVSKAYA

*(Communicated by I. I. Schmalhausen, Member of the Academy, 30. XII. 1940)*

On the basis of the existing conceptions of cell development (ontogeny) it is assumed that an antagonism exists between the regeneration processes and the development of malignant tumour (1). Regeneration as a restoration process of lost parts of the organism, as a healing process of wounds, of defects, is characterized by the formation of strictly typical tissues, of parts of organs, of whole organs, or systems. In tumour development a biologically opposite process takes place, the growth of the tissue being atypical.

According to the concepts of this laboratory, a factor of any nature (physical, chemical, biological), by constantly desorganizing the normal structural and physiological relations between cells and tissues, is liable to create precancerous conditions or to induce tumour development. There is always sufficient cell material for a tumour to develop, thus there is no need to have recourse to the idea of «embryonic» cells, of «reserve» cells, allegedly producing material for the tumour, if one is to adopt the point of view (1) that there must be a stage in the life of every cell capable of division (evidently directly after division), when it shows relatively little differentiation as compared with the subsequent periods of development and when this differentiation depends on the influence of the neighbouring cells, tissues, and of the organism as a whole.

If the processes of regeneration and that of the development of tumours are antagonistic indeed, then the agents inducing the development of experimental tumours should evidently be able to inhibit the regeneration process. In fact, B. P. Tokin (1) observed cancerogenic substances to inhibit the regeneration process in axolotls and hydras. As material for the present investigation served white mice, rats and guinea pigs. Tar was used as cancerogenic substance in all the experiments. The following technique was applied. The hair was pulled off or shaved on both sides of the animal, and incisions in the shape of equal squares were made with a scalpel or sharp scissors. The wound on the right side was daily smeared with tar and served as experiment, while the wound on the left side served as control. Smearing was made so as not to produce any additional trauma. The rate of healing of the wounds was carefully watched.

In the series of experiments with the guinea pigs the strips of skin excision equalled $12 \times 12$ mm. The operation was not carried out under sterile condition, however, the skin was smeared with rivanole on both sides. In

order to compare the degree of healing, transparent paper was used for outlining the contours of the lesions. This, as well as other procedures applied in surgical practice, supplied sufficient material for comparison.

Experiments on Mice. A total of 83 mice were used as test objects. The first series involved 5 mice. Skin excisions in the shape of squares were made on the right and left sides. The wounds on the right sides were smeared with tar for 7 days following. The healing of the wounds was rapid; that of the right (experimental) side took place more slowly. By the 11th day, after the wounds had completely healed, similar lesions were repeated and the wounds of the experimental side were invariably smeared with tar. By the 5—6th day in three cases out of five the margins of the control wounds were found to have contracted considerably as compared with the experimental side, and the skin surrounding the wounds showed no departure from the norm, whereas the skin surrounding the experimental wounds assumed a bluish tint and peeled. By the 11th days after repeated wounding in 4 experimental cases out of five the wounds healed more slowly as compared to the control. Where complete healing was observed, the skin was smooth except for a small scab. The four experimental wounds were under a scab.

On the 12th day after the renewed trauma the same five mice were subjected to a third wounding, and the experimental wounds were continuously smeared with tar. By the third day it became evident on four mice that the regeneration of the experimental wound was considerably lagging as compared with the control. This can be seen from the results of measurements (Table 1).

A total of 57 mice served as test objects in the second series. The technique was similar to that applied in the first series, but no renewing of the wound was practiced. On the third day of the experiment the wound margins began to draw together in the majority of cases, the process being more intense on the control than on the experimental side. In 12 test mice out of 57 a complete contraction of the margins took place in the control wounds, while the experimental wounds were still gaping. In five mice of these twelve the control wounds had completely healed, while the experimental showed gaping wounds after the scab was taken off. In 15 mice the margins of the control wounds had almost grown together, the control wounds being still of considerable size. In 15 cases a considerable difference was noted between the area of the right and left wounds, the left, control, area being considerably smaller. In two mice the control wound was but slightly smaller than the control. In twelve mice out of 57 no great difference was found between the healing rate of the control and experimental wounds. In one mouse a reverse picture was observed—the healing rate of the experimental wound was somewaht higher than that of the control.

The conclusions to be drawn are the following: in the majority of cases the healing of the skin lesion lags behind that of the control wounds under the influence of cancerogenic substance.

In the third series seven 21-day-old mice had been used as test object. Experiments similar to the above-mentioned were carried out. On the third day after wounding and regular smearing a complete healing of the control wound could be observed in five mice out of seven. On the experimental side—a considerable unhealed wounded area. In one mouse positive result was not quite obvious, and, finally, in one case no differences in the healing rate were noticed.

In the fourth series five mice were experimented on. The treatment was somewhat different. Tar was daily rubbed into the hairless right side of the mouse. For five days the hair continued growing. On the 8th day the hair began shedding on all the smeared skin regions. In three mice considerable

peeling of the skin was observed over rather large regions. Subsequently, in a number of cases the skin began to chap. On the 11th day of tar application skin excisions were made (as in the preceding series).

The picture of healing is a most diverse one. In three mice no difference was found between the healing rate of control and experimental wounds. In one mouse—an obvious positive result was obtained: the control wound had healed and the wounded area was covered with hair, whereas the experimental wound had not healed. In one mouse a reverse result was obtained. After all the wounds had healed, the wounds were renewed. On the third day the wound margins were observed to draw nearer in the control series (for measurement result see Table 2). In all cases positive results were obtained.

Table 1

| Nos. of mice | Size of experimental wounds on the 3rd day of healing in mm | Size of control wounds on the 3rd day of healing in mm |
|---|---|---|
| 1 | 6 × 9 | 2 × 10 |
| 2 | 7 × 9.5 | 4.5 × 9.5 |
| 3 | 7.5 × 8 | 1.5 × 8 |
| 4 | 4 × 7 | 7 × 6 |
| 5 | 1.5 × 9 | 1.5 × 8.5 |

Table 2

| Nos. of mice | Size of experimental wounds in mm | Size of control wounds in mm |
|---|---|---|
| 1 | 4.5 × 8 | 3 × 4 |
| 2 | 7.5 × 7 | 5.5 × 6.5 |
| 3 | 5 × 6 | 3 × 5..5 |
| 4 | 6 × 8.5 | 2.5 × 8.5 |
| 5 | 6 × 8.5 | 2.5 × 8.5 |

On the third day after measurement in three cases out of five a retardation of healing was observed in the control wounds, while in the other two healing was found to proceed at the same rate as before.

Series 5 included nine mice. Application of tar to the skin of the right side was practiced for 17 days. On the 4—5th day after application skin peeling was observed on the entire treated area (especially pronounced in four cases), as well as the appearance of small ulcerations. Prolonged application of tar resulted in pronounced peeling of the skin which grew markedly red at the same time. In one case a scab formed on the large treated area. On the 17th day after tar application lesions were made and smearing was stopped. The expected result was not obtained. This should evidently be explained by the fact that tar was applied on a large area, up to the back, and the treatment might have affected the skin of the control side. However, it is possible that the tar was not only mechanically transferred, but that the cancerogenic substance had affected the organism as a whole.

Experiments on Rats. Seven one-month-old rats were used as test objects. On the fourth day of the experiment two rats out of the seven showed a considerably better healing of the left control side as compared to the experimental wounds. In three rats the area of the right and of the left wounds was almost equal. In two rats the control wounds were somewhat larger than the experimental ones. Final results of the experiment: in four rats out of the five the control side was completely healed, whereas on the experimental side the regeneration process was still in progress. Two rats perished before the final results were obtained, in one rat a reverse picture was observed.

Experiments with Guinea Pigs. A total of 10 guinea pigs were used to clear up the action of tar on the healing process of wounds The technique applied was similar to that used on other objects. On the third day after the operation a more intense healing rate of the control wounds was observed as compared with the experimental wounds. This became still

more illustrative during the following days. On the 10th day the following conditions of the healing wounds were observed in some characteristic cases.

No. 1. Experimental side: shrivelling up and peeling of the skin around the wounded area. No hair growth. The wound is gaping and bleeding. Process of epithelization scarcely noticeable if any. Area of the wound—19×14 mm. Control side, the hair growing. Surface of the wound dry. Wound area much smaller than that of the experimental wound, 7×7 mm.

No. 2. Area of the experimental wound 16×10.5 mm, of the control wound—6×3.5 mm.

No. 3. Experimental side: poor hair growth. The skin surrounding the wound has shrivelled up and is peeling strongly. No epithelization. Control side: good hair growth. The margins of the wound considerably drawn together. A scab has formed on the surface.

Total results of experiments on guinea pigs. In 9 guinea pigs out of 10 the healing rate of the control wound is higher than that of the experimental wound. This is especially evident from the measurements of the wound area on the 10th day of healing. One case seems to have yielded negative results. On the 15th day all the 10 guinea pigs gave a positive result, i. e. healing of the control wounds took place much more intensely than that of the experimental wounds, as shown by the measurements of the wound areas.

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*EXPERIMENTELLE MORPHOLOGIE*

# DIE BIOLOGISCHE WIRKUNG DES β-IONONS UND DES IONZITS (ZERFALLSPRODUKTE VON VITAMIN A)

Von M. L. ROCHLINA und A. A. BODROWA

*(Vorgelegt von I. I. Schmalhausen, Mitglied der Akademie, den 28. XI. 1940)*

Das β-Ionon wurde 1893—98 von Tiemann entdeckt. Es geht in den Bestand des Moleküls des Vitamin A ein, hat aber nach den Literaturangaben keine vitaminartige Wirkung. Im Prozess der Synthese von Vitamin A und den ihm verwandten Verbindungen, für welche als Ausgangsprodukt β-Ionon diente, wurde von Prof. Balachowsky und Wulfsohn eine neue hoch-molekülare Verbindung, ein Produkt der Kondensation des Ionons, erhalten, das von den Autoren Ionzit genannt wurde. Die vorliegende Untersuchung hat die Aufgabe die biologische Wirkung des β-Ionons und des Ionzits zu prüfen.

Der Einfluss des β-Ionons und des Ionzits auf die Regeneration der Axolotlextremitäten. Die Versuche wurden an 30 Axolotln, gleichen Alters, mit einem Gewicht von 2.8—4 g ausgeführt, die in 5 gleiche Gruppen eingeteilt waren. Allen Axolotln wurde die hintere linke Extremität am Kniegelenk amputiert. Die Versuchstiere fühlten sich wohl und zeigten während der Versuchszeit eine Gewichtszunahme. Die Versuchsbedingungen und die erhaltenen Resultate sind in der Tabelle angeführt.

Der Einfluss des β-Ionons und des Ionzits auf die Regeneration der hinteren Axolotlextremität

| No. der Gruppe | Stadium der Regeneration / Bedingungen in denen die Axolotl gehalten wurden | Auftreten der Regenerationsstadien in Tagen | | | | | Die mittlere Gewichtszunahme in % |
|---|---|---|---|---|---|---|---|
| | | I Blastem | II Kegel | III Platte | IV Skelettanlage | V Fingerbildung | |
| I | Reines Wasser (Kontrolle) | 9.5 | 30 | 44 | 51 | 66 | 111.6 |
| II | β-Ionon, 0,5 mg % | 7.3 | 22.8 | 32 | 42 | 56 | 91.6 |
| III | β-Ionon, 1 mg % | 8.3 | 26.8 | 39.2 | 50 | 63.6 | 91.0 |
| IV | Ionzit, 0,5 mg % | 9.66 | 28.1 | 38.1 | 44.3 | 59.3 | 99.1 |
| V | Ionzit, 1 mg % | 10.3 | 28.0 | 37.0 | 47.0 | 63.0 | 81.6 |

Die Beschleunigung der Regeneration, wie dies aus der Tabelle zu ersehen ist, verläuft gleichmässig auf allen Stadien. Der Umstand, dass die Regene-

ration in unseren Versuchen langsamer verlief, als dies der Fall bei Weiss war, erklären wir dadurch, dass unsere Versuche während des kalten Winters 1940, wo die mittlere Zimmertemperatur niedrig war, ausgeführt wurden. Die Axolotln wurden in Wasser mit Zimmertemperatur gehalten.

Von sehr grossem Interesse ist, dass die geringere Konzentration von β-Ionon, 0.5 mg%, einen stärkeren Einfluss auf die Regeneration ausübte, als eine höhere Konzentration von 1 mg %. Das Ionzit hatte eine analoge Wirkung auf die Regeneration der hinteren Extremität, allerdings war die Konzentration von 0.5 mg% weniger effektiv, als die entsprechende Dose von β-Ionon, und die Regeneration endete am 59. Tag, d. h. 7 Tage früher, als bei der Kontrolle. Die Konzentration des Ionzits (1 mg%) hatte auf die Regeneration dieselbe Wirkung, wie die entsprechende Dose von β-Ionon.

Der zweite Versuch wurde an 24 Axolotln mit einem Gewicht von 11—12 g angestellt. Die Amputation der hinteren Extremität wurde ebenso, wie im ersten Versuch, am Kniegelenk ausgeführt. Ausser den Konzentrationen von β-Ionon, die in dem ersten Versuch verwendet wurden, wurde noch eine geringere Konzentration—0.2 mg% von β-Ionon—geprüft. Die zweite Versuchsserie wurde in den Monaten April und Mai angestellt, und im Zusammenhang mit der höheren Luft- bezw. Wassertemperatur verlief der Regenerationsprozess bedeutend schneller.

Das V Regenerationsstadium wurde bei den Axolotln, welche in reinem Wasser gehalten wurden, im Mittel nach 37.1 Tagen erreicht. Bei Axolotln, die sich in einer Konzentration von β-Ionon mit 0.2 mg% und 0.5 mg% befanden,wurde dasselbe Stadium im Mittel nach 30.3 und 30.6 Tagen erreicht, d. h. um 7 Tage früher als bei der Kontrolle. Die Konzentration von β-Ionon mit 1 mg % war auch in diesen Versuchsserien weniger effektiv. Das V Regenerationsstadium wurde im Mittel nach 32.3 Tage erreicht, d. h. nur um 4.8 Tage eher als in der ersten Gruppe.

Die Resultaten dieses Versuchs bestätigen voll und ganz dieselben des ersten Versuchs. Also, haben β-Ionon und Ionzit eine beschleunigende Wirkung auf die Regeneration: in beiden Versuchen bei 42 Axolotln unter dem Einfluss von β-Ionon und Ionzit regenerierten die Extremitäten schneller als bei den 12 Kontrolltieren, wobei der Effekt der Wirkung von der verwendeten Dose abhängt.

Die antithyreoidine Wirkung des β-Ionons und des Ionzits im Prozess der experimentellen Metamorphose der Axolotln. Das im Wasser aufgelöste pulverisierte Thyreoidin ruft in kurzer Zeit die Metamorphose der Axolotln hervor. Eine wässerige Kolloidlösung von Karotin, welche in das Wasser gebracht wird, hemmt die Wirkung des Thyreoidins und damit auch die Metamorphose, wobei der Grad der Hemmung von der Konzentration des Karotins abhängt (²).

Wir haben nach derselben Methode Versuche angestellt, um die antithyreoidine Wirkung des β-Ionons und Ionzits an Axolotln zu prüfen. Die erste Gruppe von Axolotln wurde im Wasser gehalten, wobei 5 mg Thyreoidin zu 100 cm³ Wasser zugefügt wurde. Die Metamorphose der Axolotln war bis zum 25. Versuchstage beendet. Die II und III Gruppe der Axolotln erhielten dieselbe Konzentration von Thyreoidin mit Zugabe von β-Ionon (0.5 mg %—II Gruppe und 1 mg%—III Gruppe). Vorher wurden im Verlauf von 70 Tagen diese Axolotln bei derselben Konzentration β-Ionon gehalten. Die Metamorphose wurde bei allen Axolotln gehemmt, und endete im Mittel in der II Gruppe 3 Tage und in der III Gruppe 4 Tage später. Also hat das β-Ionon eine leichte hemmende Wirkung auf die Metamorphose.

Die nächste Serie wurde angestellt um die antithyreoidine Wirkung des Ionzits zu prüfen. Die I Gruppe von Axolotln bekam dieselbe Dose von

Thyreoidin (5mg auf 100 $cm^3$ Wasser). Die Metamorphose endete in 16—17 Tagen. Die II und III Gruppe von Axolotln wurden ins Wasser gebracht unter Zugabe derselben Dose Thyreoidin (5 mg) und Ionzit (Konzentration 0.5 mg%), wobei die Axolotln der III Gruppe vorher im Verlauf eines Monats bei Konzentration von 0.2 mg% β-Ionon gehalten wurden. Das Ionzit hatte eine aktivere antithyreoidine Wirkung, als das β-Ionon. In der II Gruppe hat das Ionzit eine Hemmung der Metamorphose fast um 7 Tage hervorgerufen. In der III Gruppe äusserte sich die Hemmung der Metamorphose noch stärker, im Mittel um 11—12 Tage. In der I Gruppe war die Metamorphose der Axolotln zum 16 Tage schon beendet, während die Axolotln der III Gruppe erst die I Phase erreichten.

Hieraus folgt, dass das β-Ionon und das Ionzit eine antithyreoidine Wirkung besitzen. Da diese Produkte zugänglicher sind und ihre Herstellung billiger zu stehen kommt, können sie in der Klinik gegen Hyperthyreose angewendet werden. Wir können noch bemerken, dass in der Klinik des Prof. Wowsy von Dr. Litwak positive Resultate erhalten wurden bei der Anwendung des β-Ionons gegen die Hyperthyreose.

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*ENDOCRINOLOGY*

# FORMATION OF SPERMATOZOA IN CULTURES OF RAT TESTICLES AS INFLUENCED BY THE HYPOPHYSIS

By N. DIOMIDOVA

*(Communicated by I. I. Schmalhausen, Member of the Academy, 30. XII. 1940)*

Most of the authors ([2],[3]) assert that hypophysal hormones [prolan Au 13 ([1])] do not affect the rate of maturation of spermatozoa. There are, however, some positive data as to the effect of the hypophysis on the growth of spermatozoa in vivo ([4]) as well as in tissue cultures ([5]).

While studying the regularities of spermatogenesis in vitro I have found ([6]) that notwithstanding complete isolation of testicles from the integral influence of the organism as a whole, the maturation rhythm of sperm cells remained undisturbed. The spermatogenesis in testicles of 30-day-old immature rat males proceeds at the same rate in vitro, as within the organism, except the final stage af formation of the head of sperm cells. In order to find out the possible rôle of the hypophysal hormone in the process of formation of spermatozoa, I carried out a series of experiments, in which testicles of immature rat males and hypophysal tissue obtained from mature males were cultivated at the same time.

The tissue culture method described in our previous communication([6]) made it possible to test the immediate effect of the hypophysis upon spermatogenesis. A small portion of hypophysis was cultivated during one series of experiments, while in the second an entire hypophysis was imbedded into the medium. A total of 15 testicles were examined, among which 6 were cultivated simultaneously with a whole hypophysis, while 9 were cultivated at the same time with a portion of it. The observations lasted 15—20 days. One testicle for each animal was fixed before the beginning of the experiment, the other after the experiment. As fixative 10% formalin was used. From the sections were made counts of the canaliculi cuts at different stages of maturity of sperm cells (Table 1).

Histological investigation of the gonads showed that 7 days after the beginning of the experiment the maturity grade proved to be similar in both culture series, that containing an entire hypophysis and a portion of the hypophysis. Table 1 shows that the percentage of vasa efferentia containing dividing spermatocytes is the same as at the beginning of cultivation (incubation). Neither does spermatid number increase during the 7-day-long cultivation in vitro. 20-day-old testicle cultures combined with portions of the hypophysis also failed to show any acceleration of the rate of separate stages of spermatogenesis. Table 2 shows that increase in the number of spermatids can be stated not until the 15th day in the series of cultures with an entire hypophysis, this indicating that a progressive course of spermatogenesis is going on.

Table 1

State of Testicles Cultivated Simultaneously with Hypophysis

| Nos | Spermatocytes | | | | Maturation division | | | | Spermatids | | | | Growth of culture in days |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Control* | | Experimental | | Control | | Experimental | | Control | | Experimental | | |
| | Number | % | Number | % | Number | % | Number | % | Number | % | Number | % | |
| 13 | 359 | 93.0 | 532 | 89.8 | 11 | 2.9 | 15 | 2.6 | 16 | 4.1 | 45 | 7.6 | 20 |
| 14 | 166 | 72.8 | 359 | 65.6 | 9 | 4.0 | 22 | 4.1 | 53 | 23.2 | 166 | 30.3 | 20 |
| 18 | 371 | 92.0 | 292 | 79.5 | 11 | 3.0 | 16 | 4.2 | 20 | 4.9 | 60 | 16.3 | 20 |
| 32 | 268 | 80.2 | 333 | 69.3 | 5 | 1.6 | 14 | 2.9 | 61 | 18.2 | 133 | 27.8 | 8 |
| 33 | 130 | 56.7 | 203 | 52.8 | 5 | 2.3 | 24 | 6.4 | 94 | 41.0 | 157 | 40.8 | 7 |
| 1 | 490 | 98.7 | 381 | 96.4 | 7 | 1.3 | 3 | 0.8 | — | — | 11 | 2.8 | 7 |
| 2 | 553 | 94.8 | 337 | 93.3 | 12 | 2.2 | 8 | 2.3 | 18 | 3.0 | 16 | 4.4 | 7 |
| 3 | 565 | 92.7 | 399 | 90.0 | 14 | 2.4 | 13 | 3.0 | 30 | 4.9 | 31 | 7.0 | 7 |
| 4 | 325 | 78.6 | 379 | 79.5 | 16 | 4.0 | 11 | 2.5 | 72 | 17.4 | 86 | 18.0 | 7 |
| 7 | 589 | 99.1 | 420 | 88.6 | 5 | 0.9 | 6 | 1.3 | — | — | 48 | 10.1 | 7 |
| 8 | 307 | 81.8 | 370 | 83.7 | 6 | 4.5 | 10 | 2.3 | 50 | 13.7 | 62 | 14.0 | 7 |
| 29 | 292 | 96.6 | 416 | 87.3 | 5 | 1.7 | 19 | 4.7 | 5 | 1.7 | 43 | 9.0 | 15 |
| 34 | 412 | 96.7 | 438 | 85.8 | 5 | 1.2 | 17 | 3.5 | 9 | 2.1 | 55 | 10.7 | 15 |
| 37 | 320 | 88.4 | 399 | 76.7 | 11 | 3.1 | 13 | 2.6 | 31 | 8.5 | 108 | 20.7 | 15 |
| 40 | 270 | 90.0 | 437 | 86.0 | 8 | 2.7 | 9 | 1.8 | 22 | 7.3 | 62 | 12.2 | 15 |

Table 2

| Cultivation length | | Maturation division | | | Spermatids | | |
|---|---|---|---|---|---|---|---|
| | | $M \pm m$ contrs. | $M \pm m$ experim. | $M_1 - M_2 \pm \pm \sqrt{m_1^2 + m_2^2}$ | $M \pm m$ contrs. | $M \pm m$ experim. | $M_1 - M_2 \pm \pm \sqrt{m_1^2 + m_2^2}$ |
| 7 days | Portion of hypophysis | 2.55±0.58 | 2.03±0.32 | 0.52±0.65 | 6.5±2.32 | 9.8±2.38 | 3. 3±3.32 |
| 7 days | Whole hypophysis | 1.95±0.32 | 4.65±1.74 | 2. 7±1.77 | 29.6±11.4 | 34.3±16.4 | 4. 7±19.9 |
| 20 days | Portion of hypophysis | 3. 3±0.35 | 3. 6±0.53 | 0. 3±0.63 | 10.7±2. 2 | 18.1±6.51 | 7. 4±6.87 |
| 15 days | Whole hypophysis | 2.17±0.43 | 3.15±0.62 | 0.98±0.75 | 4.9±1.49 | 13.15±2.56 | 8.25±2.96 |

Similar progressive spermatogenesis occurred when immature testicles without the addition of hypophysis were cultivated in usual medium ([6]). None of the testicles cultivated yielded any transformation of spermatids or formation of the head of sperm cells. Investigation of the hypophysis structure 14 days after the beginning of cultivation revealed considerable disturbances in the normal structure, even leading to complete degeneration of all the tissues. The peripheral region of the hypophysis becomes destroyed as a rule and the cells perish. Nearer to the centre of the hypophysis only eosinophilic cells containing nuclei at different stages of degeneration were observed but once.

Basophilic cells become destroyed to such an extent that it is scarcely possible to find any traces of them. Their nuclei do not stain at all.

The intensive degeneration of basophilic cells is evidently accompanied with isolation of the cell hormones liberated into the medium. As it is known, Windsor, Cutting and Reed Lewis ([7]) cultivated during 80 days small bits

of the anterior lobe of a rat hypophysis in rotating tubes. The nutritive fluid was removed every 5 days and injected into virgin guinea pigs. Examinations of the females showed that the stimulating effect of the medium upon the endocrin and sexual glands became evident when the fluid used was taken from 14—15-day-old cultures. The hypophysis studied at this time showed every sign of autolysis. The authors express the opinion that cell destruction results in the liberation of the hormone present. This conclusion makes me believe that the hypophysal hormone was present already in 15-day-old culture and could produce its specific effect. Thus, although the testicles of immature rats were exposed for 14 days to the action of the hypophysal hormone, no manifestation of any stimulating effect upon separate stages of spermatogenesis and spermatozoa formation could be observed, while the same testicles non-separated from the organism would surely be able to produce spermatozoa within the period mentioned above.

The hormone of the hypophysis stimulates a metabolic change of the sperm cells resulting in cell division ([8]). The action of the hypophysal hormones may be compared with an impulse stimulating the spermatogenesis at a certain stage of gonad differentiation, whereafter the process having started once, develops automatically and does not depend on the location of the testicle within the organism or in a nutritive medium ([6]).

The fact that the hypophysis has some influence upon the spermatogenesis only on a certain stage of gonad differentiation, is confirmed by experiments, in which the hypophyses of animals of different ages were ectomised. The removal of the hypophysis at early stages of development eliminated in females the 1st maturation division of the oocytes in follicles which did not yet contain any follicular secret. Now, in the case of males the process does not go beyond the first pachytene stage in the prophase, upon which spermatogenesis stops altogether ([8]). Martinovich ([9]) who also cultivated testicles of new born rats and mice, also reports that development in isolated testicles stopped at the pachytene stage.

So far as the differentiation of the sperm cell is concerned, it is evident that acceleration of maturation of spermatozoa depends on other factors which need further investigations, whereas the hypophysal hormones do not play any decisive rôle in this process.

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*PALEONTOLOGY*

# A NEW UPPER CARBONIFEROUS GENUS *DAIXITES* FROM THE FAMILY *MEDLICOTTIIDAE* KARPINSKY

By V. E. RUZHENCEV

*(Communicated by A. A. Borissiak, Member of the Academy, 12. I. 1941)*

For the last years our conceptions regarding the family *Medlicottiidae* have greatly gained in scope owing to the discovery of many new forms. Particular attention attracted the new genus *Prouddenites* Miller met in the Upper Carboniferous and first described in 1930. At that time Miller characterized this genus as the most primitive possible stage in the development of the family *Medlicottiidae*. The nearest descendant of *Prouddenites* has been so far believed to be the Upper Carboniferous genus *Uddenites*, which has attained a higher stage of phylogenetic development. However, the collection of ammonites from the Upper Carboniferous of South Urals contains specimens belonging to a new very interesting genus which occupies in the phylogeny an intermediate position between *Prouddenites* and *Uddenites*. For this genus the author suggests the name

*Daixites* gen. nov.*

D i a g n o s i s. Conch discoidal, very involute, with lateral sides flat, venter rounded. Ratio of the height of the whorl to its width 2.6—2.8. Sculpture consists of the most delicate transverse striae, forming on the lateral side two arches: one curved forward on the umbilical half, and the other one turning backwards on the ventral half. Suture complicated, consisting on the external side of a ventral, 9 lateral and one umbilical lobe, and on the internal side—of a dorsal and 6 lateral lobes. The fourth external lateral lobe corresponds strictly with the first internal lateral one. Ventral lobe trifid. First lateral lobe very wide, asymmetrically bipartite; its wider but less deep outer branch is, in turn, asymmetrically bifid. All the remaining lateral lobes, both external and internal ones, are entire. Dorsal lobe long, bifid, deeply penetrating into the preceding septum. First and second lateral saddles very conspicuous by their large dimensions, the second one being even somewhat higher than the first one. The second internal saddle is obviously underdeveloped as compared to the two neighbouring ones. Base of the first lateral lobe is much lower in position than that of the second lateral.

Genotype. *Daixites meglitzkyi* gen. et sp. nov.

R e m a r k s. The described genus was formerly designated by the author as *Prouddenites*, since by a number of characters it shows indeed some resemblance to the latter. It is especially noteworthy that in both cases the first lateral lobe has a similar, though not quite identical outline. However, at the first glance it seems to be obvious that the Uralian species is distinguished from the only American species by a considerably flatter conch. A detailed study of characters brought forth still many more distinctions which will be indicated below.

* *Daix*—old Greek name for the Ural river.

Generally speaking, the genus *Prouddenites* bears considerable resemblance to *Neopronorites*, although its entire habitus is somewhat different. But what is most conspicuous on comparison of the two aforementioned genera, is the fact that the first lateral lobe in *Neopronorites* is symmetrically bifid, whereas in *Prouddenites* it is sharply asymmetrical, divided into two parts, the outer one being much wider than the inner one. It is the appearance of this new feature, entirely alien to all the representatives of the family *Pronoritidae*, which testifies, in the author's opinion, to a qualitative leap to a new stage in the phylogenetic development. A symmetrical bipartite division of the first lateral lobe is observed in all the representatives of the family *Pronoritidae* throughout the beds from the Lower Carboniferous up to the Lower Permian inclusively. This persistent character having been disturbed, the way was open, as a result of natural selection, to vigorous formation of new genera, in which the system of characters mostly subject to hereditary variability is exactly the one genetically and topographically connected with the first lateral lobe (the external saddle, ventral margin in the shell). In the Upper Carboniferous alone there appeared, as a result of the disturbance of the former conservative system, four genera: *Prouddenites*, *Daixites*, *Uddenites* and *Artinskia*. Yet, in order to bring more clarity into the subject of our further discussion, it should be emphasized that the most primitive of the enumerated genera, *Prouddenites*, has still preserved some important features typical of the family *Pronoritidae*: it has the bases of the first and second lateral lobes situated at the same level; the first lateral saddle is always higher than the second one.

The genus *Daixites* has acquired a number of characters leading to an entirely new structure, sharply distinguished from that of representatives of the family *Pronoritidae*. At the same time *Daixites* is quite clearly demarcated from *Prouddenites*. Their principal differences are as follows: the shell in *Daixites* is laterally considerably more compressed; the ratio of the height of the whorl to its width attains in this case 2.6—2.8, whereas in *Prouddenites* the corresponding ratio does not exceed 1.8. The former exhibits 9 lateral lobes, the latter no more than 7, the seventh one partly passing into the umbilical wall. The outer branch of the first lateral lobe in *Daixites* obviously tends to become shorter, this tendency being the more emphatic, the older the shell. The base of the inner branch of the first lateral lobe in representatives of the new genus is definitely lower in position than the base of the second lateral lobe. The second lateral saddle has not only attained the dimensions of the first one, but has in quite mature specimens even surpassed it in growth. All the peculiarities of the genus *Daixites* referred to above have persisted or undergone further development in *Uddenites*. However, the last-mentioned genus is sharply distinguished from our new genus in: 1) the appearance of the ventral furrow, 2) further reduction of the outer part of the first lateral lobe and 3) sharp lengthening of the ventral lobe. Thus, phylogenetically the genus *Daixites* occupies an intermediate position between *Prouddenites* and *Uddenites*. At the same time by the general character of its suture and of the shell as a whole (a great number of sutural elements, large dimensions of the second lateral saddle, flatness of conch) the newly established genus shows no resemblance whatever to the representatives of the family *Pronoritidae*. On the contrary, the general configuration of its suture and the arrangement of separate sutural elements exhibit such characters as are peculiar to many representatives of the family *Medlicottiidae*.

*Daixites meglitzkyi* gen. et sp. nov.

S h a p e (Fig. 1, *a*, *b*). Conch flat, discoidal, very involute. Ventral side rounded. Lateral sides nearly flat, only feebly convex in the middle portion,

markedly convergent toward the umbilicus, not sharply separated from the ventral side. Umbilical walls very narrow, steep, with a fairly sharp umbilical shoulder. Umbilicus very narrow, not increasing with growth. In mature individuals some quite essential modifications are observed. With shell diameter of about 30 mm and more, there appears on the lateral walls, near the ventral side, a quite distinct concave zone. At diameter equal to about 40 mm and more a ventral furrow can be observed, this being not very sharp, but still fairly discernible.

Fig. 1. *Daixites meglitzkyi* gen. et sp. nov. Ventral and lateral views of holotype (×1). Ural river, Upper Carboniferous.

S c u l p t u r e. Owing to the poor state of preservation of the test layer, no details of the sculpture are visible. There may be observed but the finest transverse striae with rather complicated curves on the lateral wall. On the umbilical half of the latter they form an arch bent forward, on the ventral half—a sinus, the most concave part of which coincides with the zone of maximum convexity of the lateral wall.

S u t u r e (Fig. 2, *a—f*). Ventral lobe trifid; its lateral indentations acuminate, the middle one basally broad, nearly rectangle. First lateral lobe

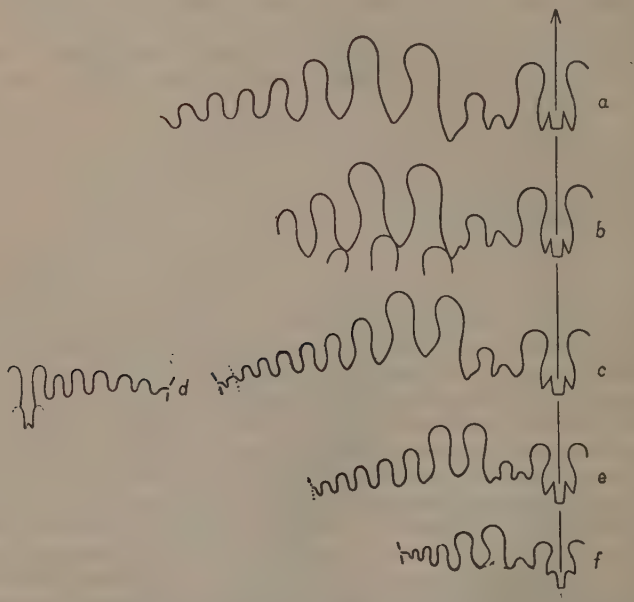


Fig. 2. *Daixites meglitzkyi* gen. et sp. nov.: *a*—at *H*=16.0 mm (×3) (holotype); *b*—at *H*=about 14.5 mm (×3); *c*—at *H*=13.0 mm (×3); *d*—internal suture of the same specimen at *H*=about 19.0 mm (×3); *e*—at *H*=8.0 mm (×3); *f*—at *H*=3.5 mm (×6). Occurrence: *a—e*—Ural river; *f*—Sakmara river. Upper Carboniferous.

very broad, entirely asymmetrical, deeply divided into two differently outlined branches. Outer branch wide, asymmetrically bifid, with inner indentation narrow and outer one—wide; these indentations are always obtuse

at the base. Inner branch of the first lateral lobe narrow, wholly asymmetrical, in some cases entire, in others bifid, with outer prong underdeveloped. In mature specimens this branch is considerably longer than the outer one. The dividing saddle is rounded at the top and somewhat compressed in the middle. All remaining lateral lobes are undivided; the second, third and fourth of them are somewhat asymmetrical, lanceolate, blunt-tapering, the rest being more symmetrical, rounded. The base of the second lateral lobe is situated far above the base of the first one. The number of lateral lobes totals nine. The umbilical wall displays one more lobe. The external saddle is not high, properly rounded. The first lateral saddle is much higher, slightly asymmetrical. The summit of the second lateral saddle is still higher. The third lateral saddle is much smaller than the preceding one.

Dorsal lobe narrow, very long, bifid, reaching far into the preceding septum. The internal lateral lobes are six in number; they are all appreciably shorter, entire, basally rounded. The first and second internal lateral lobes are paired with the fourth and fifth external lateral ones. The saddle dividing the first two internal lateral lobes is less developed than the two adjacent saddles.

| Dimensions: | *D* | *H* | *W* | *Du* | *H*:*D* | *W*:*D* | *Du*:*D* | *H*:*W* |
|---|---|---|---|---|---|---|---|---|
| I | 44.5 | 26.1 | 9.2 | 2.4 | 0.59 | 0.21 | 0.05 | 2.84 |
| II | 31.2 | 18.3 | 6.7 | 2.8 | 0.59 | 0.21 | 0.09 | 2.73 |
| (Holotype) III | 29.0 | 16.6 | 6.3 | 2.4 | 0.57 | 0.22 | 0.08 | 2.63 |

Remarks. *Daixites meglitzkyi* sp. nov. is so far the unique representative of the genus. In what it differs from the representative of the most closely allied genus *Prouddenites* has been shown in the generic characteristic.

Occurrence. 9 specimens were found on the right bank of the Ural river, 2.5 km north-west of the Iliinskaia village. One specimen was met along the Sakmara river, in a 165 km railway excavation. Upper Carboniferous.

The specific name is given in honour of the geologist Meglitzky, who together with Antipov soon after the publication of Murchison's work for the first time questioned the correctness of synchronizing the greater part of the terrigenous series occurring between the Ural and Sakmara rivers with the Artinskian sandstones.

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*PALEONTOLOGY*

# THE FIRST REPRESENTATIVE OF THE GENUS *EMILITES* RUZHENCEV IN THE UPPER CARBONIFEROUS OF THE URALS

By V. E. RUZHENCEV

*(Communicated by A. A. Borissiak, Member of the Academy, 12. I. 1941)*

In 1917, Emil Böse (1) described an interesting form *Paralegoceras incertum* Böse, met in the Upper Carboniferous (Gaptank formation) of Western Texas. In 1932, Miller (2) referred the same species to the genus *Metalegoceras*. In 1937, Plummer and Scott (4) reported that *Paralegoceras incertum* seems to them to be a poorly preserved specimen of *Glaphyrites kansasensis* (M. et G.). In 1938 Ruzhencev (5) arrived at a conclusion that the species in question bears no relation to any of the above-mentioned three genera, and that it should be regarded as the most primitive representative of the family *Adrianitidae*. To designate this primitive Upper Carboniferous group of adrianitids a new generic name *Emilites* [genotype—*Emilites incertum* (Böse)] was introduced. The diagnosis of this new genus was based entirely on literary material, which was no difficult task, since Böse gave a detailed characteristic of «*Paralegoceras*» *incertum*, pointing out all the typical features of this original species. In 1940, Miller and Furnish (3), in turn, came to a conclusion that «*Paralegoceras*» *incertum* belongs to a special genus for which they suggested the name *Plummerites*. However, this genus was referred by the American authors with no argumentation to the family *Gastrioceratidae*. In conformity to the rules of nomenclature, the name *Plummerites*, as one introduced at a later data, is to be placed in the synonymy.

There is no doubt whatever that the genus *Emilites* is the most primitive representative of the family *Adrianitidae*. At the early stages of development the shell of *Emilites* has a globose, perfectly involute shape, just like the successive members of the same phylogenetic series, *Crimites* and *Neocrimites*. A peculiar feature of the sculpture of the genus *Emilites* consists in the transverse scalloped ribs which are no less typical of the genus *Crimites*. Along the umbilical shoulder of the conch of *Emilites* runs a characteristic thickening of the test layer; a similar thickening is observable in representatives of the genera *Crimites* and *Neocrimites*. And lastly, all the peculiarities of the suture in *Emilites* likewise connect this genus with other representatives of the family. Indeed, the presence on the external wall of the conch of two lateral lobes, corresponding strictly with two internal lateral lobes, is typical of our genus. Such stage of development is observed in very young individuals of *Crimites*, *Neocrimites* and *Adrianites* (3,6,7). The general outline of sutural elements in the genera *Emilites* and *Crimites* is quite uniform, the only difference being that in the former case each side of the conch has two external and two internal lateral lobes, whereas in the latter case—three external and three internal ones, arranged in connected pairs.

In 1940 the author collected in the Chkalov region a few specimens of the genus *Emilites*, deserving to be separated as a new species, the description of which is given below.

*Emilites plummeri* sp. nov.

S h a p e. Conch at the neanic stage globose, in the maturity inflated-ellipsoidal, involute, with an almost closed umbilicus (Fig. 1, *a*, *b*,). The ventral side and lateral walls are smoothly confluent, forming a regular semi-cylindrical surface. Umbilical walls narrow, overhanging. Umbilical shoulder quite sharply traceable. Whorl crescentic in cross-section; external and internal walls of conch greatly convergent umbilically.

S c u l p t u r e. Unfortunately, the preservation of the material is such as to render a study of all the peculiarities of the sculpture impossible. However, in some specimens it has been possible to distinguish faint traces of transverse scalloped ribs. No constrictions are observed, as a rule. Only in one case a faint constriction can be seen, forming on the ventral side a small curve directed toward the aperture of the conch.

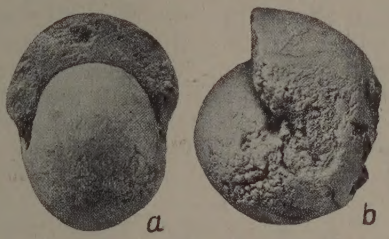


Fig. 1. *Emilites plummeri* sp.nov. Ventral and lateral views of holotype (×1.5). Ural river, Upper Carboniferous.

S u t u r e (Fig. 2, *a*, *b*). Ventral lobe divided by a rather high, medially compressed ventral saddle into two branches pointed at the base. In width they do not differ from the dividing saddle. First lateral lobe broad, nearly symmetrical, basally acuminate, assuming on the whole a bell-shaped outline. Second lateral lobe still broader, entirely asymmetrical, roughly speaking, funnel-shaped, occasionally bearing on the inner side one or even two additional prongs. Thus, this lobe may be entire,

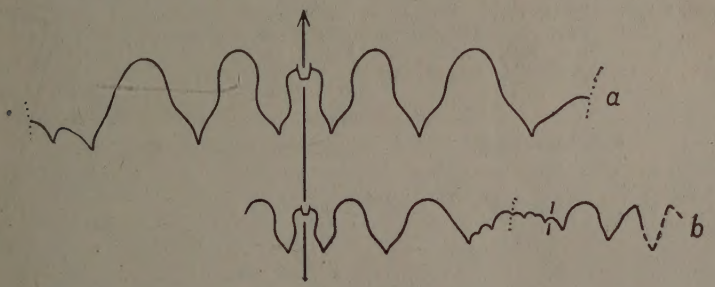


Fig. 2. *Emilites plummeri* sp. nov.: *a*—external suture of holotype at $W=11.0$ mm (×4); *b*—external and internal sutures of paratype at $W=8.8$ mm (×4). Ural river, Upper Carboniferous.

bifid or trifid. Well developed umbilical lobes—none. Interspace between second external and second internal lateral lobe accomodates a broad, but not high saddle notched with a few minute prongs, or incipient umbilical lobes. Dorsal lobe narrow, rather wedge-shaped. First internal lateral lobe shorter, bell-shaped. Dividing saddle pointed at the top. Second internal lateral lobe feebly developed; rather wedge-shaped in outline.

| Dimensions: | *D* | *H* | *W* | *Du* | *H*:*D* | *W*:*D* | *Du*:*D* |
|---|---|---|---|---|---|---|---|
| (Holotype) | 20.6 | 16.1 | 11.5 | 1.0 | 0.78 | 0.56 | 0.05 |

Remarks. In literature there has been known but one representative of the genus *Emilites*, described by Böse under the name of *Paralegoceras incertum* Böse, and by Miller and Furnish ([3]) as *Plummerites incertus* (Böse). On comparing it with *Emilites plummeri* sp. nov., we note that there is much resemblance between them both in the shape of the shell and outline of the sutures. However, note should be taken of some quite essential differences. It has been reported by Miller and Furnish that in *E. incertus* a faintly prominent crest runs along the umbilical shoulder (it is well seen in Fig. 2, table 30); its presence has likewise been indicated in the first description by Böse. No traces of any such complication in the umbilical region of the shell are observed in *E. plummeri*. Some differences may as well be noted in the outline of the sutures of the two species under comparison. Particular attention deserves the fact that the branches of the ventral lobe in *E. incertus* are nearly half as wide as the ventral saddle in *E. incertus*, whereas in *E. plummeri* they are of equal width. Details in configuration of the broad umbilical saddle differ in the two cases concerned. However, hardly any importance is to be attached to this fact, considering the great individual variation of the suture in the umbilical region in the genus *Crimites*, the nearest descendant of *Emilites*. It is more important to point out another distinction, bearing upon the inner portion of the suture: in *E. incertus* the summit of the first internal saddle is rounded, in *E. plummeri* it is obviously acuminate.

Occurrence. 25 specimens were found in the Chkalov region, on the right bank of the Ural river, 2.5 km north-west of the village Iliinskaia. Upper Carboniferous.

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